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CHEMISTRY

FOR

ENGINEERS AND MANUFACTURERS.

VOL. I.—CHEMISTRY OF ENGINEERING, BUILDING, AND METALLURGY.

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS.

A PRACTICAL TEXT-BOOK.

BY

BERTRAM BLOUNT, F.I.C., F.C.S., Consulting Chemist to the Crown Agents for the Colonies.

AND

A. G. BLOXAM, F.I.C., F.C.S., Consulting Chemist, Head of the Chemistry Department, Goldsmiths' Inst., New Cross.

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1. Chemistry of the Chief Materials of Construction.
2. Sources of Energy.
3. Chemistry of Steam-raising.
4. Chemistry of Lubrication and Lubricants.

II. METALLURGICAL PROCESSES used in the Winning and Manufacture of Metals.

VOLUME II.

THE CHEMISTRY OF MANUFACTURING PROCESSES.

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XVI. Leather, Glue, and Size.
XVII. Explosives and Matches.
XVIII. Minor Chemical Manufactures.

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With Illustrations.

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PREFACE.

In writing the present book the authors have had chiefly in view the needs of Practising Engineers, Managers of Works, and Technical Students desirous of obtaining some knowledge of Chemical Technology.

In a book of this scope, lengthy descriptions of plant and of processes which differ from each other merely in detail would be out of place. For this reason, only such processes are described as are typical of the class to which they belong.

The adoption of this plan has given opportunity for presenting the subjects dealt with in a manner which shows their relations to each other. It is hoped, therefore, that the book as a whole may prove useful even to the expert in any one of the subjects touched upon. In order to achieve this degree of usefulness the authors have specially endeavoured to explain the general principles underlying each process, even when the working details appear complex and arbitrary.

Vol. I. includes the chemical principles of subjects which are of particular interest to the Mechanical Engineer, to

the Architect and Builder, and to all Manufacturers who are concerned in the erection of plant and the production of power. The information given is designed to be of so practical a character as will enable an owner of machinery or user of power to detect causes of bad economy, and to realise when saving may be effected by calling in expert assistance.

Vol. II. treats of the chief manufactures which have a chemical basis. The authors trust that for many readers, especially students of manufacturing chemistry, the information given will be found adequate to afford a sound groundwork of knowledge without proving as difficult to grasp as is the mass of facts proper to a monograph.

LONDON, *December*, 1895.

CONTENTS.

PART I.

INTRODUCTORY.

CHAPTER I.

Chemistry of the Chief Materials of Construction.

	PAGE
Stone, Brick, and Concrete—	
Siliceous Stones, . .	1
Calcareous Stones, . .	4
Bricks, ...	6
Concrete, Cement, Mortar,	9
Testing Hydraulic Cements,	11
Structural Metals—	
Cast Iron, ...	13
Wrought Iron, . . .	15
Ingot Iron and Mild Steel,	18
Copper and its Alloys, Brasses and Bearing Metals, ...	20
Aluminium, Nickel, . .	24
Roofing Materials—	
Slates and Tiles, . .	25
Galvanised Iron, Tinned Iron, ...	26
Strength, Permanency, and Preservation of Materials—	
Table of Strength of Building Stones and Metals, .	28
Permanency of Structural Materials, Weathering, Welding, Brazing, and Soldering, Corrosion of Metals, ...	31
Preserving Structural Materials, Special Preservative Paints, Timber Preservation, . .	42

CHAPTER II.

The Chemistry of the Sources of Energy.

Solid Fuels—	
Coal, Calorimetry, . .	50
Coke, ...	53
Brown Coals and Peat, Briquettes, . . .	55
Wood and Charcoal, . .	56
Liquid Fuel—	
Petroleum, . . .	57
Gaseous Fuel—	
Coal Gas, ...	60

	PAGE
Producer Gas, Regeneration, Smoke Prevention,	63
Water Gas,	69
Semi-water Gas,	71
Natural Gas,	73
Hydrogen,	74
Oxygen,	75
Electrical Heating,	77
Measurement of Temperature—	
Thermometers and Pyrometers,	79
Industrial Temperatures,	85
Direct Conversion of Chemical into Electrical Energy—	
Galvanic Cells,	86
Storage cells,	90
Gas Batteries,	92
Natural Forms of Kinetic Energy—	
Water Power, Tides, Wind,	93
Transmission of Energy,	96

CHAPTER III.

The Chemistry of Steam Raising.

Water—	
Hard Calcareous Waters,	99
Soft Waters,	101
Saline Waters, Sea Water,	101
Boiler Incrustations, Corrosion of Boilers,	104
Softening and Purification of Boiler Water—	
General Considerations,	108
Clark's Process,	108
Boiler Compositions,	112

CHAPTER IV.

The Chemistry of Lubricants and Lubrication.

Liquid Lubricants—	
Fatty Oils,	114
Mineral Oils,	117
Mixed Oils,	118
Solid Lubricants,	119
Corrosion induced by Lubricants,	120

PART II.

METALLURGY.

	PAGE
Metalliferous Ores—	
Metallurgical Processes,	124
Sizing and Concentration,	124
Roasting and Calcination,	124
Reduction,	125
Refining,	125
Iron—	
Iron Ores,	126
Principles of Iron Extraction,	129
Preparation for Smelting, Magnetic Concentration,	129
Reduction in Blast Furnaces,	130
Hot Blast Stoves,	132
Chemistry of the Blast Furnace,	134
Classification of Kinds of Iron,	138
Purification of Crude Iron, Puddling,	139
The Bessemer and Open Hearth Processes, Basic Processes,	142
Crucible Cast Steel, Case Hardening, Harveyising,	147
Effect of Foreign Elements upon Iron and Steel, Manganese Steel,	148
Copper—	
Copper Ores,	154
The Welsh Copper Smelting Process,	154
The Mansfeld Process,	163
Bessemerising Copper,	163
Wet Processes of Copper Extraction,	165
Electrolytic Winning and Refining of Copper,	166
Copper Alloys,	169
Lead—	
Lead Ores,	170
Self-reduction of Galena,	172
Reduction of Oxidised Ores by Carbon, Bessemerising Lead,	175
Reduction of Galena by Iron,	175
Refining and Desilverising Lead,	176
Lead Alloys,	180
Zinc—	
Zinc Ores,	181
Winning and Refining of Zinc,	182
Uses and Alloys of Zinc,	184
Cadmium,	185
Tin—	
Tin Ores,	185
Winning and Refining of Tin, Tungstate of Soda,	185
Uses and Alloys of Tin,	188
Antimony,	188
Bismuth,	191
Nickel—	
Nickel Ores,	193
Winning and Refining of Nickel,	194
Properties and Uses of Nickel,	197
Cobalt,	197
Mercury—	
Distillation of Mercury from Cinnabar,	198
Properties and Uses of Mercury,	202
Silver—	
Silver Ores,	202

	PAGE
Dry Processes for Winning Silver,	204
Wet Processes for Winning Silver,	206
Properties and Uses of Silver,	209
Gold—	
Concentration of Gold Ores,	210
Winning Alluvial Gold,	210
Winning Gold from the "Ore,"	211
Winning Gold by Chemical Processes, Chlorination, Cyanide Process,	213
Refining and Parting of Gold,	215
Platinum Group of Metals,	216
Metals Difficult of Reduction—	
Aluminium,	219
Magnesium,	223
Manganese,	224
Sodium and Potassium,	224

INDEX, ... 227

CHEMISTRY

FOR

ENGINEERS AND MANUFACTURERS.

VOL. I.

CHEMISTRY OF ENGINEERING, BUILDING, AND METALLURGY.

CHAPTER I.

THE CHEMISTRY OF THE CHIEF MATERIALS OF CONSTRUCTION.

THE permanency of a given structure and the degree in which it is fitted for its use, do not depend exclusively upon the mechanical strength of the materials composing it, but are largely influenced by the chemical composition of these materials and by the chemical conditions to which they are exposed. It follows, therefore, that a knowledge of the chemistry of the chief materials of construction is necessary in deciding of what material a given structure is to be built.

STONE, BRICK, AND CONCRETE.

A rough classification of natural stones used at all largely for building purposes, may be made by dividing them into the groups *siliceous* and *calcareous*. The following are brief descriptions of the chief building stones commonly used:—

1. **SILICEOUS STONES.** — **Sandstone** is composed of grains of quartz (*silica*) cemented together to form a coherent mass. Its value as a building material depends largely on the substance cementing the grains of quartz together, as on the removal of the agglutinant, disintegration of the stone naturally follows. The nature of the agglutinant varies considerably. Siliceous matter itself sometimes constitutes the cement and

the stone is then a mass of nearly pure silica, and is both refractory to weathering and difficult to work. An argillaceous cementing material (composed essentially of silicate of alumina) is more easily attacked than a siliceous agglutinant, and the sandstones containing the former are, therefore, less refractory to weathering than those held together by the latter. A special form of sandstone, laminated by layers of micaceous matter, is that known as *Yorkshire flagstone* and used for street paving and making acid-proof apparatus—*e.g.*, chlorine stills (*q.v.*, Vol. II.). For the latter purpose the laminar character of the stone and its freedom from cementing material other than siliceous matter constitute the advantages which it presents. Felspar also occurs as a cementing material of sandstone. (When the felspar is more or less decomposed into kaolin the sandstone falls into the argillaceous category.) Much *millstone grit*, which is a coarse grained sandstone, very tough and resistant, is thus cemented. Other cementing materials of less importance are oxides of iron, giving the sandstone a yellow, brown, or blue colour, according to the state of oxidation of the iron. The presence of iron pyrites, which sometimes occurs in sandstone, tends to bring about the disintegration of the stone on weathering by the oxidation of the pyrites. Sandstones cemented with iron oxides are less permanent in character than those held together by siliceous agglutinants. Barium sulphate has also been found to exist as a cementing material of certain sandstones.

A cementing material comparable in importance with those of the siliceous class, is the calcareous matter frequently found fulfilling this function. Such sandstones are held together by calcium carbonate and are more readily worked than the siliceous variety, coming in this respect under the head of *free-stones—i.e.*, stones which can be easily sawn and wrought into shape without chipping and grinding. Such sandstones are, however, somewhat easily attacked by weathering, as will be explained at the end of this chapter. Besides the cementing material of a sandstone, the size and shape of the constituent grains are of importance in influencing the character of the stone. Thus, in sandstone of ideal quality from the point of view of mechanical strength and non-porosity, the grains should be of such assorted sizes as to leave a minimum amount of space either unoccupied or filled by the cementing material. The statement that the coarser the grain the more durable the sandstone (other things being equal), is not based on satisfactory experimental evidence. With regard to resistance to weathering, especially to the action of frost, it has been recently shown that a less porous stone is not necessarily more resistant than one more porous, as the latter allows room for the expansion of the absorbed water in freezing and suffers less disintegration (*v.i.*). Obviously, this possession of spaces capable of affording room for

expansion in freezing may compensate for the tendency of such a stone to absorb and hold a large quantity of water. The following analyses of sandstone grits are typical :—

	Grit, Cambrian (Barmouth).	Carboniferous Millstone Grit (Cumberland).
Moisture,	0·125	0·050
Combined H_2O,	0·935	1·290
SiO_2,	80·600	87·400
Al_2O_3,	9·200	3·997
CO_2	1·025	1·876
P_2O_5,	0·076	Trace.
SO_3,	Trace.	0·060
Fe_2O_3,	Trace.	...
FeO,	2·370	1·366
MnO,	0·232	0·279
FeS_2,	...	0·300
CaO,	1·330	1·932
MgO,	1·285	0·684
K_2O,	1·647	0·741
Na_2O,	1·372	0·332
	100·197	100·307
Specific gravity,	2·689	2·710

Granite consists of a mixture of *felspar* (a double silicate of alumina and potash or soda—*e.g.*, $6SiO_2 . Al_2O_3 . K_2O$—*quartz* (silica), and *mica* (a double silicate of alumina and magnesia, potash or soda—*e.g.*, $4MgO . Al_2O_3 . 4SiO_2$ *). An average proportion of these constituents is 40 to 50 per cent. of felspar and 40 to 30 per cent. of quartz, the remainder being mica. A large proportion of mica, especially in plates of an appreciable size, causes the granite to polish badly and to fade quickly. *Syenitic granites* have the mica partially or wholly replaced by *hornblende* ($[FeMg]O . SiO_2$) which is generally black in colour. It is evident that this range of composition involves a corresponding range of appearance and properties of granites. A granite containing much quartz and a stable form of felspar is refractory to destructive agencies, but hard and difficult to work. Such a stable form of felspar is generally vitreous and transparent, allowing the light to penetrate the rock and to be reflected from the darker constituents. A soft earthy felspar is opaque, and causes the granite to appear lighter in colour; hence it happens that conspicuously white granites are usually little resistant to weather. The colour of granite may vary from grey to red. The former

* The complexity of mica, owing to the replacement of one oxide by another, is such that its general formula may be written

$$4(K_2MgFe)O . (AlFe)_2O_3 . 4SiO_2.$$

colour is due to the magnesia mica (*biotite*), the latter to a red variety of potash felspar (*orthoclase*). Iron stains in the granite indicate unsoundness, and granite in which the felspar is earthy in appearance is also inferior (p. 3). Granite, being an igneous rock, that is, one which has solidified after fusion, probably under pressure, is impervious and non-porous, and suffers destruction exclusively from without. Its permanence depends on the size and degree of coherence of its constituent minerals, the close-grained kinds, formed of small interlocking crystals, being the most refractory to destructive agencies. Syenitic granites are harder and generally more durable than ordinary granites.

Gneiss, which is a granite in which the mica occurs stratified, is also used to a certain extent as a building material. *Whinstone* and *trap* (both known as "greenstone" from their colour) are also igneous rocks used for building, and consist chiefly of felspar and hornblende.

2. **CALCAREOUS STONES.—Marble** in the strict sense is calcium carbonate, approximately pure, crystallised as calcite. There is no hard and fast line between limestone and marble, but by general consent the latter term is applied to those forms of calcium carbonate which have a well-marked crystalline fracture, like that of loaf-sugar. It appears that marble has been formed geologically by the heating to a plastic condition of forms of calcium carbonate, of looser structure, under pressure sufficient to prevent the escape of CO_2, which would otherwise have been eliminated below the temperature of fusion. This change has been effected experimentally by Le Chatelier, who found it to occur at 1020° C. = 1868° F., an hour's exposure sufficing to produce artificial marble. The purest form of marble is white and without veins, *Carrara marble* serving as an example. The colours of marbles other than white are due to the presence of various impurities. Thus, ordinary white marble with dark veins is coloured with metallic oxides—*e.g.*, those of iron; red marbles are also coloured with iron as ferric oxide, and black marble owes its colour to bituminous matter, as much as 1·48 per cent. of carbon having been found in an Irish specimen. Some marbles are distinguished by markings due to enclosed fossils—*e.g.*, those from Derbyshire. In addition to the above varieties, certain siliceous stones are often commercially termed "marble," although in no sense true marble. Thus, **serpentine,** which is an hydrated magnesium silicate containing iron, is frequently called "marble," but is distinguished physically (apart from its chemical difference) by its structure, which is not crystalline. The following are analyses of serpentine:—

GREEN SERPENTINE.

	Per cent.	Per cent.*
SiO_2, ...	33·80	40·06
Al_2O_3, ...	1·65	1·37
Cr_2O_3, ...	0·42	0·20
FeO, ...	9·79	3·43
ZnO, ...	0·30	...
CaO, ...	3·46	...
MgO, ...	31·74	30·02
Na_2O, ...	0·32	...
MnO, ...	Trace.	0·09
NiO, ...	Trace.	0·71
CO_2, ...	5·66	...
Combined water, . . .	12·86	12·10
	100·00	...

Alabaster (hydrated calcium sulphate) is also termed "marble" in the trade. Marble is only used for ornamental building, except when its abundance at the spot where it is to be used makes it sufficiently cheap as a structural material. The waste of marble cutting is powdered and used for making CO_2 for preparing aërated waters.

Limestone is a compact form of calcium carbonate, ranging from a material somewhat less definitely crystalline than marble to one devoid of crystalline structure. The **carboniferous limestones** are very compact; **lias limestone** is also compact, but contains a good deal of clay (see *Cement*, Vol. II.). **Kentish rag** is a tough limestone often coloured with oxide of iron. Some varieties will not bear weathering. The structure of many limestones resembles that of sandstone, being granular; an example is furnished by **oolitic limestone**, the granules of which are large, definite, and rounded. **Portland stone** is an oolitic limestone. **Bath stone** is very variable in quality, some varieties withstanding weather well and others being easily disintegrated; it is easily worked, and hardens after exposure to air. The more nearly limestones approach marble in structure, the more durable they are. **Purbeck stone** is a shelly limestone consisting largely of small fossil shells. Besides these, which are approximately pure limestones, others are found intermixed with serpentine and similar siliceous minerals. True **dolomite** is a double carbonate of calcium and magnesium, corresponding with the formula $CaCO_3 . MgCO_3$; it ranges from this composition to that of ordinary limestone (which always contains a small proportion of magnesium carbonate); it is a hard and durable stone.

* This analysis is incomplete, but shows the characteristic constituents of a serpentine.

The nearer a **magnesian** or **dolomitic** limestone approaches the composition of true dolomite, the more durable it is.

All the above calcareous stones are from their nature less fitted to withstand the action of weak acids than are the siliceous stones previously described. The causes of their destruction will be dealt with later.

Artificial stone is considered in the section on *Cements*, Vol. II.

3. **BRICKS*** may be regarded as blocks of artificial sandstone with more cementing material than that which is present in the natural varieties. In the trade many kinds are known by name, but they cannot here be considered individually. **Kiln-bricks** are more uniformly burnt and more generally reliable than **clamp-bricks,**† which are apt to be unevenly burnt, many of them (particularly those on the outside of the clamp—"place bricks") being often soft from insufficient burning. On the other hand, those near the flue-holes of the clamp are usually over-burnt. (For the construction of kilns used in brick-burning, see section on *Clay Industries*, Vol. II.) Clamp-burnt bricks are classified according to the preparation of the clay of which they are made into **malms, washed** and **common stock.** The first-named are made from clay which has been ground with chalk, so as to make an artificial gault brick (*v.i.*); the second are made from clay freed from gross impurities by washing; and the last are manufactured from the untreated clay. Each clamp of each kind yields bricks differing in quality according to their burning, involving a further classification which is a matter of purely trade interest. The following among the less ordinary kinds require separate mention.

Red bricks are usually made from a fairly clean clay, nearly free from lime (which would produce a yellow tint), and containing a good deal—*e.g.*, 10 per cent.—of ferric oxide, to which their colour is due. The following is an example of such a clay in the air-dried state:—

	Per cent.
Insoluble silicates and sand,	39·26
Combined silica,	23·12
Alumina,	14·02
Ferric oxide,	8·39
Lime,	1·63
Magnesia,	3·45
Potash,	2·96
Soda,	0·15
Moisture,	1·68
Combined water, organic matter, and loss,	5·34
	100·00

* See also section on *Clay Industries*, Vol. II.

† The rectangular heap of bricks, itself constituting the walls and flues of the furnace, is known as a "clamp."

Gault bricks are made from gault clay, which contains some 25 per cent. of calcium carbonate. They are light in colour and easily fusible, and thus need special care in burning.

Blue bricks are made from highly ferruginous clay, the iron in which is reduced to the state of magnetic oxide in the process of burning. They are fired at a clinkering temperature, and are therefore sintered together and less porous than ordinary bricks, while their mechanical strength is greater (*v.i.*). A common kind of blue brick is only superficially "blue," having received a coating of ferric oxide previously to being burnt. Such bricks are weaker and more pervious (as soon as the outer surface is destroyed) than genuine blue bricks, which are sintered throughout their mass. The standard size and weight of a common brick are $8\frac{3}{4}$ inches × $4\frac{1}{4}$ inches × $2\frac{1}{2}$ inches, and 7 lbs. respectively. Special shapes and sizes—*e.g.*, for curved structures—are also made.

Fire bricks differ from ordinary bricks in that they are made of clay nearly free from oxides capable of acting as fluxes—*e.g.*, ferric oxide, lime, magnesia, and alkalies. There are two classes of ordinary siliceous fire bricks, viz.:—(1) Those composed of a true refractory clay (silicate of alumina), to which refractory sand or burnt refractory clay has been added to prevent undue shrinkage in drying and firing; and (2) those composed of nearly pure silica, with a minimum of foreign oxides capable of serving as cementing material. These types are illustrated by *Stourbridge* and *Dinas* fire bricks respectively; analyses of such clays are appended:—

	Plastic Fire Clay.	Dinas "Clay."
Quartz,	36·3	95·94
Combined silica,	27·0	1·68
Alumina,	23·3	1·40
Ferric oxide,	...	0·49
Ferrous oxide,	1·8	...
Lime,	0·7	0·29
Water and organic matter,	10·3	...
Alkalies,	...	0·20
	99·4	100·00

Bricks of these materials are burnt in kilns at a high temperature, in order that they may not alter in volume when in place in the furnace in which they are to be used. Dinas "clay" is found as a loose sand, and requires the addition of a small percentage of lime as a cementing material. **Ganister,** which is a similar material to Dinas clay, is found as a sandstone, and for furnace lining is generally ground and moulded *in situ*. Highly

siliceous bricks usually expand when strongly heated, whereas those made from plastic clay contract.* The size and shape of fire bricks are even more various than those of ordinary bricks, on account of the need for accurate fitting of furnace linings.

The foregoing bricks are "acid" in character—*i.e.*, being composed largely of free silica (quartz), they are capable of acting as an acid material at high temperatures, and of fluxing in contact with a basic substance, such as lime. The more nearly a fire brick approaches kaolin in composition—*i.e.*, the smaller the proportion of free silica it contains—the less marked are its acid properties and the better is its resistance to basic fluxes. On increasing the proportion of alumina until an ultimate composition corresponding with that of bauxite is reached, a nearly "neutral" brick is obtained capable of withstanding fairly the action of both acid and basic oxides. A typical composition of a **bauxite brick** is Al_2O_3 70·7 per cent., Fe_2O_3 13·6 per cent., SiO_2 15·7 per cent.

Chromite (chrome iron ore) has also been used to furnish a fairly neutral brick, having an average composition of Cr_2O_3 50 per cent., FeO 30 per cent., Al_2O_3 15 per cent., SiO_2 5 per cent. Such a material is often used on account of its approximate neutrality, in order to separate acid and basic bricks (*v.i.*) when both are used to line one furnace, the former being generally adopted for arches where mechanical strength is necessary, and the latter for bottom linings where basic materials have to be fused, or (as in a steel furnace) where a basic action has to be exerted.

Carbon bricks have been prepared from retort carbon, ground, mixed with tar, and burnt; they are not only neutral in character but have little tendency to alter in volume in the furnace, and are bad conductors of heat.

Soapstone (magnesium silicate, $6MgO.5SiO_2.2H_2O$) has also been used as a neutral furnace lining; it is, however, attacked by basic materials.

Basic bricks, which are largely used in steel making by the basic process, are prepared either from dolomite (double carbonate of calcium and magnesium), or from magnesite (magnesium carbonate). The former substance, though burning to a hard and refractory state, slowly slakes and disintegrates on exposure to air; the latter is free from this defect. Both substances are more commonly used to line furnaces *in situ* by ramming the crushed material, mixed with tar, so as to form a layer on the surface of the bottom. Actual bricks are usually prepared from precipitated magnesia, moulded under heavy pressure and burnt at a high temperature. The best form of crude magnesia for basic bricks is that prepared by calcining

* Such bricks require an allowance of one-eighth of their linear dimensions for shrinkage in drying and burning.

Styrian magnesite, and has the composition—MgO 77·6 per cent., CaO 7·3 per cent., Al_2O_3 and Fe_2O_3 13·0 per cent., SiO_2 1·2 per cent. The impurities present aid the sintering of the brick to a compact mass. Magnesia, when "dead-burnt" at a high temperature, is devoid of plasticity, and in order to be moulded must be mixed with half its volume of lightly burnt magnesia, or a little magnesium acetate or chloride. Magnesia bricks do not flux with acid bricks below 1,600° C. = 2,912° F., but above that temperature slag readily; their behaviour with neutral alumina bricks is similar. They are used for lining basic steel furnaces, cement kilns, furnaces for reburning strontia in sugar works (see *Sugar*, Vol. II.), and for lead smelting works, being tight to that metal and to its oxide which readily penetrates acid bricks. Although all fire bricks (acid and basic) are commonly termed refractory, yet the term is over-wide unless the conditions under which the bricks are to be used are specified. Such bricks may be properly termed infusible—*i.e.*, at industrial temperatures. It is proper to observe that there is a difference between infusibility and refractoriness. Both "acid" fire bricks, *i.e.*, those consisting mainly of silica, and "basic" bricks, *e.g.*, those composed of lime and magnesia, are infusible at any temperature commonly employed, but they may only be called refractory when the conditions under which they are used are accurately defined. Thus acid bricks are unattacked by silica and acid silicates, but are corroded by mixtures containing a preponderance of basic oxides, the reverse being true of basic bricks (*cf.* the remarks on the subject under *Cement*, Vol. II.).

4. **CONCRETE** consists of a mixture of "cement mortar" with an "aggregate." By cement mortar is meant a mixture of sand and cement, as distinct from one of sand and lime constituting common mortar. The aggregate is simply some form of broken stone or pebbles that happens to be readily available at the place where the mortar is made. The advantage of concrete over all other building materials is that usually only one (and that the least weighty) of its constituents has to be brought from a distance—viz., the cement. The concrete is either made in blocks * near the place of use, and slung into position, or laid *in situ*—that is, placed when freshly mixed and still plastic in its ultimate position as part of the structure. An extreme form of such adaptation is afforded by "grouting," in which a thin cement mortar is forced as a semi-fluid to fill spaces not otherwise accessible. With regard to the sand used in making cement mortar, it may be said that it should be sharp, fairly coarse, clean, and free from clay, loam, or peat. The aggregate must be chemically indifferent to the cement, and must have a fairly high compressive strength. It should preferably be in angular fragments of

* Huge blocks of concrete, which may be regarded as artificial monoliths, are much used in heavy harbour work.

irregular size, and with a moderately rough surface, to favour the adherence of the cement. Clean "burnt ballast,"* fragments of hard limestone, granite chippings, broken brick, and the like are serviceable as aggregates. The proportion of sand to aggregate and of cement to both must be so adjusted that unfilled spaces between adjacent fragments of aggregate may be as few and small as possible, and the concrete block "solid" throughout. With aggregate and sand of ordinary quality a mixture of 1 part of cement, 2 of sand, and 4 of aggregate by volume makes a good concrete, though frequently mixtures much poorer in cement are used. In making concrete, thorough mixture of the ingredients must be secured, and the water must be added by sprinkling, so as to get the mass uniformly wet. A porous aggregate may require previous wetting to ensure the presence of sufficient water for the setting of the cement, and the surface to which the plastic mass is to be applied may also need wetting for the same reason. Regard must be had to the setting time of the cement (which varies largely with different specimens, *v.i.*), in order that the concrete may be got into place before setting has begun; otherwise, the half-set cement will be disturbed and its coherence impaired. Recently the *Monier system* of building construction has been introduced on the Continent and in this country. The objection to concrete for purposes where a space has to be spanned—viz., that its tensile strength is comparatively low—is removed in the case of this system of construction, which consists in the use of interlacing iron rods imbedded in cement mortar or concrete, by means of which the high tensile strength of the former and the high compressive strength of the latter are taken advantage of. The system is adapted for the erection of fire-proof buildings, light bridges of moderate span, and for the manufacture of pipes of large diameter.

The cement used in making concrete is necessarily not an **aerial cement** such as common mortar. By an **aerial cement** as distinct from an **hydraulic cement** is meant one that hardens by exposure to air. the hardening being due to desiccation and carbonation. In the heart of a concrete block both operations would occur so slowly as to prevent setting in a reasonable time. Moreover, common aerial mortar is too weak mechanically to bear the large dilution with inert sand and aggregate, which is perfectly suitable for a strong hydraulic cement. Moreover, much concrete is used under water, and its cement portion must be unattacked by water after the first hydration, which causes its setting. The cements used for concrete are therefore always strong hydraulic cements. **Portland cement** is most largely employed, though **Roman cement, puzzuolana cement, slag cement,** and **hydraulic lime** are also thus utilised. (For a description of the manufacture and cause of setting of these

* This material is burnt clay: "Thames ballast" is gravel.

cements, see the section on *Cement*, Vol. II.) Besides being used for making concrete, cement is employed for preparing cement mortar—*i.e.*, ordinary mortar with the lime replaced wholly or partly by cement. It is used in the same way as common mortar where extra strength or resistance to water is required. It is also used for facing work, lining tanks and reservoirs, &c., on account of its imperviousness. "Neat" (unmixed) cement is but little used, as when spread as a facing it is liable to crack from irregular contraction.

Ordinary **mortar** should be made from good "fat" lime (see *Lime*) and sharp sand (1 : 3 by vol.), free from loam and earthy matter. Cow hair is often incorporated to aid its coherence, and indeed is sometimes used with cement mortar. Much benefit is claimed to be exerted upon the quality of lime mortar by the admixture of about 5 per cent. of plaster of Paris. This admixture is said to hasten the setting of the mortar and to increase its strength.

The chief necessities, other than the character of the aggregate, for the production of good concrete, are that the cement should be used in fair quantity (*e.g.*, 1 of cement to 6 of aggregate plus sand by vol.), and that it should be sound and strong. These qualities are ascertained in the following way :—

TESTING HYDRAULIC CEMENT.—The criteria which are generally determined are :—

1. **Fineness.**—The cement is sifted through standard sieves, and the percentage of residue remaining on these ascertained. A good finely-ground Portland cement should have a residue not exceeding 10 per cent. on a sieve having 76 meshes per linear inch, made of wire having a diameter of 0·005 inch, and about 1 per cent. on a sieve having 50 meshes per linear inch, made of wire having a diameter of 0·007 inch. Much modern cement is even more finely ground than this.

2. **Weight per Bushel.**—Portland cement is tested for the weight of a standard bushel, filled with the cement under definite conditions, the usual figures ranging from 108 to 115 lbs. per bushel. The object of this test is to detect underburnt cement, which is lighter and packs less closely than cement from well-burnt clinker. The test is not a good one, owing to the fact that the weight per bushel varies with the fineness of the cement apart from its quality in other respects. Thus, a cement leaving a residue of 10 per cent. on a 76 sieve will weigh about 108 to 110 lbs. per bushel, and one leaving 10 per cent. on a 50 sieve will weigh 114 to 116 lbs. per bushel.

3. **Specific Gravity.**—Fresh, well-burnt Portland cement has a specific gravity of at least 3·15, and the specific gravity may be as high as 3·19. When aerated by exposure to air the specific gravity may fall to 3·10, underburnt cements falling below this. The test is a better criterion of quality than is the determination of the weight per bushel.

4. **Setting Time.**—Hydraulic cement varies greatly in setting time—from five minutes to several hours. The setting is generally retarded by aeration, for this slakes the calcium aluminate on which the initial setting depends (see *Cement*, Vol. II.). The setting of cement is ascertained by applying a standard "needle"—*i.e.*, a steel point of definite area loaded with a given weight. When the point ceases to make an impression, the cement is considered set. An apparatus for taking an autographic record of the setting time of cement has been recently devised.

5. **Tensile Strength.**—This is determined by gauging cement, either neat or mixed with a definite weight of standard sand*

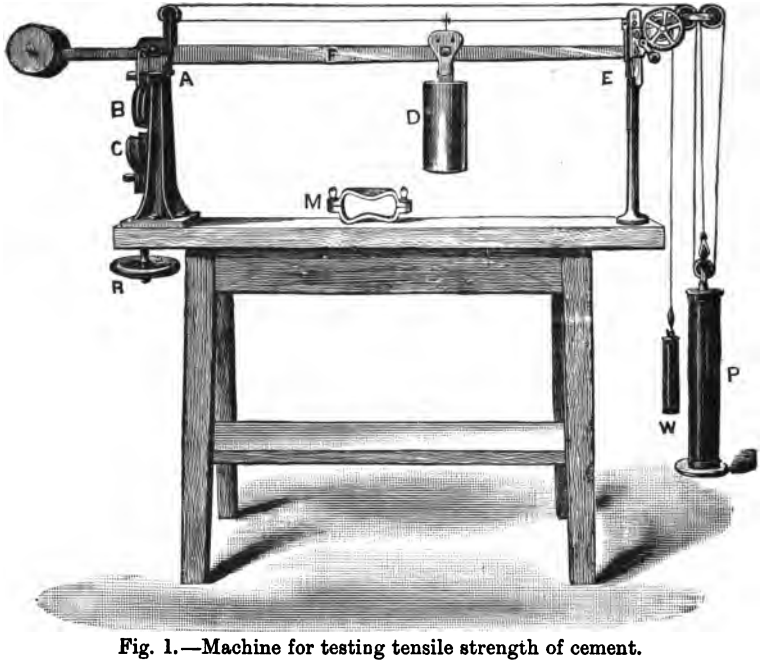


Fig. 1.—Machine for testing tensile strength of cement.

A, Standard; F, steelyard; B, C, clips; M, mould for briquette; D, weight; W, weight; P, dash-pot; R, wheel; E, end of steelyard.

(twice or thrice the weight of the cement) with water to a stiff paste, and filling it into moulds of the shape shown at M in Fig. 1. After the elapse of a definite period (usually four, seven, fourteen, or twenty-eight days), during which the "briquettes," as they are termed, are kept under water or in air, they are broken in tension by a machine similar to that shown in Fig. 1, where A

* By standard sand is meant clean sharp washed sand of even size such that the sand will pass through specified sieves.

is a standard carrying a steelyard, F, from which is suspended a clip, B, below which a second clip, C, is attached to a small horizontal hand wheel, R, serving for adjustment; the briquette, shaped in the mould, M, is held in these clips and load applied to it by traversing the weight, D, along the steelyard, this operation being performed at a uniform speed by means of the weight, W, and the dash-pot, P; this last consists of a cylinder filled with oil and fitted with a piston in which is a small hole, so that the movement of the piston as the weight falls is controlled by the slow passage of the oil from one side of the piston to the other. The waist of the briquette is of known size, usually 1 × 1 inch (= 1 square inch section) or $1\frac{1}{2}$ × $1\frac{1}{2}$ (= $2\frac{1}{4}$ square inch section). The clips that hold the enlarged ends of the briquette are best lined with rubber blocks to prevent fracture at the point in contact with them. The briquette is broken by the pull exerted by the lever of the testing machine as the weight is run out. Fracture occurs at or about the waist of the briquette, and the result is calculated from the area of the waist and from the breaking strain, and stated in lbs. per sq. in. An automatic brake is sometimes provided at the end of the steelyard, E, which stops the weight, D, on the fracture of the briquette, and so avoids the need for constant attention on the part of the operator. A cement of good quality should have a tensile strength of at least 350 lbs. per sq. in. when tested neat at 7 days, or 150 lbs. per sq. in. when mixed with three times its weight of standard sand and tested at 28 days. Finely-ground cements will give a higher sand test.

6. **Soundness.**—A cement complying with the foregoing tests is not necessarily sound. An unsound cement sometimes appears sound for weeks after it has been used, and then expands and "blows," causing injury and destruction to the work in which it has been used. The soundness of cement is generally determined by observing the behaviour of a thin pat on a glass plate kept in water for twenty-eight days; it should neither crack nor buckle. Time can be saved and a more rigid scrutiny effected by one or other of the so-called "hot tests," in which the test pieces are kept at elevated temperatures, under definite conditions. Such tests, like others applicable to materials of construction generally, are best performed by experts rather than attempted by the user of the material, as he seldom possesses the requisite apparatus, knowledge, and experience; they should never be omitted for buildings of any importance.

STRUCTURAL METALS.

IRON.—Iron is used as cast iron for columns, pillars, bedplates, frames, and standards of machinery, and as wrought iron and steel for girders, roofs, bridges, rails, boilers, and the moving parts of machinery. The production and varieties of cast iron

are dealt with in the section on this material (see *Metallurgy*). The variety known as grey cast iron is that most frequently used for the production of castings, but mottled is employed when castings of special strength are required. The former has a uniform grey fracture in which the graphite can be seen; the latter is mottled in fracture, as its name implies.

The fusibility of cast iron is closely connected with the condition of the carbon which the metal contains (see *Iron* in section on *Metallurgy*). Foundry pigs Nos. 1, 2, and 3 are grey irons, decreasing in content of graphite (and consequently in greyness of fracture), and also in fusibility, as the numbers rise. They increase in combined carbon, and consequently in hardness, in the same order. The medium quality of these three is the best for castings which are to possess considerable strength without undue brittleness. Good cast iron has a tensile strength of 7 tons per square inch, and a compressive strength of 40 tons per square inch. It is comparatively rigid and capable of little flexure or extension, and is, therefore, mainly used in compression. Where it is advantageous to have a hard wearing surface —*e.g.*, in tramway crossings, trolley wheels, or rollers—the casting is chilled by forming that part of the mould which corresponds with the portion to be chilled of massive metal, so that the cast iron is solidified rapidly and retains much combined carbon, thus acquiring extreme hardness.

Contrariwise, when it is required to confer softness and toughness on light cast iron articles of complex form, malleable castings are produced by imbedding the articles in hæmatite and heating them for some days. (For the *rationale* of this process see the section on *Metallurgy*.) The strength and reliability of cast iron depend upon its composition and the care and skill used in its casting. Analyses of a good strong foundry iron and of one containing more phosphorus and silicon, and therefore less strong but more fluid in casting, are given below.

	Foundry Iron No. 2.	Cleveland No. 3.
Graphitic carbon, ...	2·68	3·70
Combined ,, ...	0·45	0·30
Silicon, ...	1·72	2·50
Manganese, ...	0·54	0·72
Phosphorus, ...	0·68	1·50
Sulphur, ...	0·04	0·04
Iron, ...	93·89	92·00

The specific gravity of ordinary grey cast iron is about 7·1.

With regard to these figures it may be said that if special strength be required the silicon should not exceed 2 per cent., nor the phosphorus 1 per cent. When intricate castings of small

strength, but accurate outline, are to be made the amounts of both silicon and phosphorus may be nearly doubled. It is better to remelt the iron that is to be used for castings than to tap it directly from the blast furnace. The remelting is conducted in a cupola, which is an upright cylindrical furnace provided with a blast and filled with mixed coke and pig, the iron settling as a liquid in what corresponds with the crucible of a blast furnace, and being tapped when the casting is to be made. During the remelting some of the silicon in the iron is oxidised and combines with the small quantity of lime added as a flux. At the same time a little sulphur is acquired by the iron from the fuel. Thus it happens that a soft iron is hardened by remelting, although this may be carried far enough to deteriorate the iron. The reason for the hardening which arises from the elimination of silicon, is explained in the article on Iron (see *Metallurgy*). The quality of cast iron is sometimes improved by the addition of aluminium to the iron in the ladle, the quantity used being about 0·2 per cent. of the weight of the iron. As regards the mechanical quality of castings, they should be free from scabs and blow holes, and in important work a portion of the metal should be cast separately, as a bar, and tested. Castings are often porous, and give evidence thereof in the case of hydraulic cylinders, which frequently weep when first taken into use. Slight leakage of this sort is automatically cured by the rusting of the pores. A good casting will ring sound when struck and have sharp clean edges and a uniform fine-grained grey fracture.

Wrought Iron (puddled iron) has been largely replaced by "mild steel," that is ingot iron (*q.v.*), for heavy structural purposes—*e.g.*, for bridges, rails, and girders—but it is still used where a tough weldable material, easily wrought by the smith, is required. Its content of the impurities characteristic of iron —viz., C, Si, S, P, Mn—is not now necessarily smaller than that of ingot iron, but it is sharply distinguished therefrom by the presence in it of slag from the puddling process (see *Metallurgy*) occurring as layers between the laminæ representing the original bars of iron welded together in the process of manufacture. On account of the presence of this slag wrought iron has a stratified structure easily seen at the fracture of a test piece. The best is grey and fibrous, though frequently patches of crystalline material exist throughout the section. Various grades of wrought iron are commercially known. Thus "puddled bar"—which is not fit for structural use because of the large amount of slag which it contains (rendering it locally weak) and its imperfect fibre—is the first product of the hammering and rolling of the puddled blooms (see *Puddling*). "Merchant bar" is that which has been cut into lengths, piled and rolled into a new bar. The slag is thus expressed and the iron

rendered more fibrous. Repetitions of this process yield "best bar," "best best," and "best best best bar." The valuation of wrought iron is effected by analysis and mechanical testing. The following analyses show the ultimate composition of commercial wrought iron.

	South Staffordshire Wrought Iron.	Wrought-Iron Pipe.
Carbon,	0·06	0·027
Silicon,	0·04	0·200
Sulphur,	0·05	0·038
Phosphorus,	0·20	0·609
Manganese,	0·08	0·093
Iron (by difference),	99·57	99·033

The impurities, notably silicon, are largely present as slag (see Iron, section on *Metallurgy*), mechanically entangled in the fibres of the iron. Thus the sample of wrought-iron pipe, the ultimate analysis of which is given above, contained 1·118 per cent. of slag.

The influence of impurities upon wrought iron is similar to but smaller than that which they exert upon ingot iron, the reason for this difference being that in wrought iron the impurities are not dissolved uniformly in the unoxidised state throughout the metal, but are partly present as distinct segregations in an oxidised or slagged condition. The presence of this slag causes local weakness mechanically, but the iron itself is little affected. Thus, the amount of phosphorus shown in the first analysis given above would be most injurious in ingot iron, but is of little moment in wrought iron. Nevertheless, wrought irons containing much phosphorus—*e.g.*, 0·5 per cent.—have a higher strength than normal samples, but are lacking in ductility and toughness. Much sulphur—*e.g.*, 0·3 per cent.—has also a harmful effect, rendering the iron red-short. Silicon, other than that present as silicates composing the intermixed slag, is present in only small proportion in wrought iron. Manganese is not intentionally added to wrought iron as it is to ingot iron, and is not often present in considerable amount. In the cases in which it occurs it tends to counteract the evil effect of sulphur. With regard to the mechanical testing of wrought iron, it may be taken that it has a tensile strength of from 22 to 25 tons per square inch, and an extension of about 26 per cent. on a length of 10 inches; it has a compressive strength of 16 to 20 tons per square inch. These qualities are ascertained by means of a machine similar in principle to that described under cement testing. The test bar is gripped by its enlarged ends between wedge clips, and a pull from an hydraulic cylinder applied, the

pull being balanced by shifting a jockey weight along the steelyard of the testing machine. The position of the weight on the steelyard measures the pull requisite to effect the fracture of the specimen. In breaking a specimen of ductile material such as wrought iron, it is found that before fracture the test piece behaves as a viscous substance and flows, being drawn down uniformly until a contraction takes place at whatever point happens to be weakest, and fracture occurs. The elongation (extension) of the specimen which is thus caused is a measure of the ductility of the material. In judging this quality, regard must be had to the length of the specimen used, as it is found that of two test pieces of the same material differing in length, the shorter will give the higher percentage of elongation. Similarly, the thicker the test piece, *cæteris paribus*, the greater the percentage of elongation. The appearance of the test piece, before and after fracture, is shown in Fig. 2. The advantage

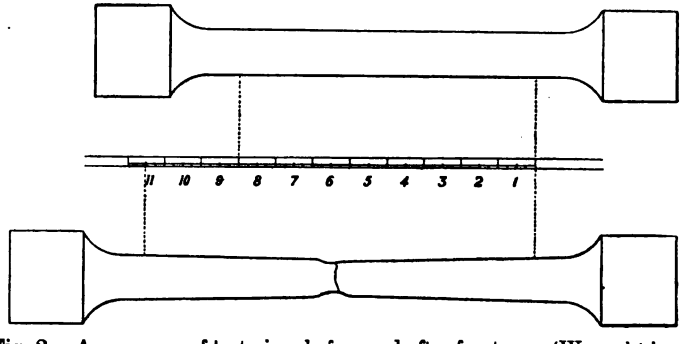


Fig. 2.—Appearance of test piece before and after fracture. (Wrought iron.)

of a ductile material such as wrought iron is that it will withstand shock, or even deformation, without sudden fracture. Those impurities which render the iron cold-short will decrease its ductility. A test frequently employed for determining toughness and ductility is the bending test, in which the test piece is bent over a bar of given radius, or even hammered down flat upon itself. The angle through which it can be bent before fracture occurs at the bend is a measure of the ductility of the material. Ductile materials, when subjected to a gradually increasing load, as in a testing machine, carry the load up to a certain point with trifling increase of their length, and on the removal of the load return to their original dimensions. On further increasing the load, the material "breaks down"—*i.e.*, begins to stretch in more marked degree, and does not "come back" on removing the load. This point is known as the "elastic limit," or more properly "yield point," and is often much below the ultimate tensile strength. Thus the yield

point of wrought iron having a tensile strength of 25 tons per square inch is about 13 tons. In considering the strength of materials for structural purposes, the yield point should be taken as a measure of their tenacity, and not the ultimate tensile strength. Ordinary practice is, however, the reverse of this. Thus the "factor of safety" of a structure is the ratio of the working load to the ultimate breaking strain, whereas it would be more rational to state it in terms of the yield point of the material. For instance, a wrought-iron girder with an ultimate tensile strength of 25 tons is said to have a factor of safety of 5 when loaded with 5 tons in tension, whereas the real factor of safety is about 2·5 with this load.

Wrought iron (in common with other structural materials) has been found susceptible of change by the application of repeated alternating stresses well below its yield point. Such stresses occur in railway axles, piston-rods, and other moving parts of machinery, and lead ultimately to the destruction of such parts. The change induced in this manner appears to be associated with a tendency of the originally fibrous material to become crystalline. The matter is, however, still the subject of investigation.

Ingot Iron and Mild Steel. — Since the device of the Bessemer and similar processes (see section on *Metallurgy*), iron containing from 0·08 to 0·6 per cent. of carbon has been prepared in ingot form and used for making girders, bridges, boiler plates, ships, rails, and steel castings. The milder grades, containing from 0·08 to 0·3 per cent. of carbon, are best termed **ingot iron**, as they lack the characteristic property of steel—viz., the capability of being hardened and tempered. The fact that manganese is used in the manufacture of these products involves the presence of this metal in the finished material and influences its hardness, manganese acting as a hardening agent in the same way as carbon, though in a smaller degree. The character of ingot iron and mild steel is best judged from its analysis; typical analyses are appended:—

	Very Mild Steel.	Mild Steel for Boiler Plates.	Bessemer Rail Steel.	Gun Steel.	Tool Steel.*
Carbon, . .	0·078	0·16	0·21	0·53	1·06
Silicon, . .	0·007	0·02	0·05	0·03	Nil.
Sulphur, . .	0·080	0·01	0·05	Trace.	0·02
Phosphorus, .	0·047	0·06	0·03	0·01	0·03
Manganese, .	0·698	...	0·36	...	0·33

It must be understood that these figures vary considerably

* Inserted for the sake of comparison; such steel is not used for structural purposes, and is made by the cementation process (*q.v.*).

with different samples, notably in the proportion of manganese, various quantities of which remain over after it has fulfilled its function in the process of manufacture. It may be taken as a rough guide that the sulphur and phosphorus in all ingot irons and steels should not exceed 0·05 per cent. The permissible limit varies, however, with the percentage of carbon; thus, although even this amount (0·05 per cent.) is most injurious to tool steel (with 1 per cent. carbon), a somewhat larger quantity (up to 0·10 per cent.) may be tolerated in ingot iron containing under 0·2 per cent. of carbon. Modern ingot iron, containing not more than 0·05 per cent. of sulphur or phosphorus and about 0·5 per cent. of manganese, will have a tensile strength of about 25 tons per square inch with 0·1 per cent. of carbon, 30 tons with 0·2 per cent., 35 tons with 0·3 per cent., and 40 tons with 0·4 per cent. The corresponding elongations on a length of 8 inches are 28, 24, 20, and 15 per cent. of the length of the specimen before fracture.

The fracture of a test piece of ingot iron or steel is distinguished from that of wrought iron by being perfectly homogeneous and silky in appearance, and free from any sign of lamination. Mild steel with a content of carbon of 0·4 per cent. has a specific gravity of about 7·89, while hard razor steel with 1·5 per cent. carbon has a specific gravity of 7·78. Steel castings, other than those of crucible cast steel, contain from 0·5 to 0·7 per cent. of carbon, and with regard to the remaining impurities are similar to ingot iron, save that 0·2 to 0·3 per cent. of silicon is sometimes added to aid in the production of a sound casting, and a portion of this remains in the finished metal. Unless subsequently forged, they are not so strong as would be rolled steel of the same composition.

Of late years several special qualities of steel containing small quantities of the less common metals have been brought into use. Thus *chromium steel* is made and used for railway tyres and for projectiles. A specimen containing 2·54 per cent. Cr and 0·39 per cent. C had a tensile strength of 44 tons per square inch and elastic limit of 24·5 tons, an elongation on 2 inches of 24·5 per cent., and a reduction of area of 33·8 per cent. Ingot iron to which aluminium has been added is not greatly different in tensile strength from ordinary wrought iron, but is said to be sounder. Thus a sample containing 0·38 per cent. Al and 0·15 per cent. C had a tensile strength of 26 tons per square inch, an elastic limit of 20 tons, an extension on 2 inches of 40·35 per cent., and a reduction of area of 60·74 per cent. *Nickel steel* finds a large use as a war material for plates and guns; a sample containing 3 per cent. Ni, 0·35 per cent. C, and 0·57 per cent. Mn had a tensile strength of 48·5 tons per square inch, with an elastic limit of 28 tons, an extension on 4 inches of 20 per cent., and a reduction of area of 42 per cent. Nickel in ingot iron has a

hardening effect up to 20 per cent., and beyond that, at the point where an iron-nickel alloy is formed, has a softening influence (see *Nickel*).

An important modified steel is so-called *manganese steel*, more properly a manganese iron alloy, the general qualities of which are described in the section on *Metallurgy*. When containing 10 to 12 per cent. of manganese it has a tensile strength of about 63 tons, an elastic limit of 30 tons, and an extension of 38 to 45 per cent.

COPPER AND ITS ALLOYS.—Iron, on account of its strength and cheapness, is used wherever possible in building construction, but for certain purposes a different material is a necessity, and such needs are filled by copper and its alloys. In the boilers of locomotives the fire-box stays and plates are generally made of copper, and the boiler tubes of brass or copper. In some cases, however, mild steel is used throughout for plates and tubes. Another large use for copper and its alloys is found in steam pipes and ships' sheathing and fittings. Copper used as such for structural purposes is always of the grade known commercially as "tough pitch" (see *Metallurgy*). The chief impurities of commercial copper of this description are As, Sb, Pb, Bi, Fe, Ni, Ag, S, and O. The composition of a modern locomotive fire-box copper plate of soft tough copper is typified by the following analysis :—

	Per Cent.
Cu,	99·50
As,	0·10
Sb,	0·01
Pb,	0·15
Bi,	0·01
Fe,	Trace.
Ni,	0·04
Ag,	Trace.
S,	Trace.
O,	0·15
	99·96

A copper of such composition will have a tensile strength of 13 to 15 tons, with an extension of 40 per cent. on a length of 6 inches.

The influence of impurities upon the tensile strength and ductility of copper depends upon the simultaneous presence of oxygen, which diminishes the deleterious influence of certain of the impurities in a marked manner. Thus, in the case of pure electrolytic copper free from oxygen, bismuth when added to the extent of 0·1 per cent. greatly lowers the tensile strength and ductility, from the formation of a fusible alloy which segregates from the bulk of the copper and destroys the homogeneity

of its structure. Arsenic and antimony, which have but little effect upon pure electrolytic copper in quantities up to 1 per cent., are usually considered injurious in copper containing oxygen. Lead, sulphur, iron, and tin have a similar effect. Nickel appears, on the other hand, to have a hardening influence, but without causing undue brittleness. When the copper, as in fire-boxes, is exposed to mechanical wear, the presence of a hardening agent is not objectionable, provided the copper remain fairly ductile. Thus it happens that old locomotive fire-boxes with much larger amounts of impurities than those quoted above have often rendered good service; one which had lasted twenty years and run 500,000 miles contained—

Cu,	98·70
Ag,	0·03
Au,	Trace.
Pb,	0·41
As,	0·37
Sb,	0·03
Bi,	0·04
Fe,	0·01
Ni,	0·30
O,	0·02 (?)
S,	0·01

Further remarks upon the influence of impurities upon copper in other respects will be found in the chapter on metals. The specific gravity of tough pitch copper, rolled or hammered, is about 8·9, varying a little with the impurities which it contains.

Another important use for copper is the manufacture of steam pipes. Small sizes may be made from solid-drawn tubes,* and are reliable up to the point calculated from the tensile strength of the metal. Larger tubes, however, are generally made by brazing together the edges of a cylinder rolled up from a piece of sheet metal. Many accidents have occurred from the bursting of such pipes. Where the failure cannot be traced to an imperfect join, it appears to be due to an alteration of the metal, probably by absorption of oxygen and sulphur, caused by its exposure to the fire during brazing. The difficulty is sometimes met by grouping several smaller solid-drawn tubes, the united cross-section of which is equal to that of the single large tube which they replace.

Alloys of copper and zinc, known generically as **brass**, are much used as structural materials. They range in composition from 90 per cent. of copper and 10 per cent. of zinc (*red metal*)

* Seamless tubes have been made electrolytically by the Elmore process, which consists in depositing copper upon a revolving mandrel while subjecting it to the pressure of an agate style, this being found to have a consolidating action.

to 60 per cent. of copper and 40 per cent. of zinc (*yellow metal, Muntz metal*). The best quality of brass where strength and ductility are required, as for locomotive tubes, contains 70 per cent. copper, 29·5 zinc, 0·3 lead, the balance (0·2 per cent.) being made up of traces of iron and other impurities. More than 70 per cent. of copper yields a somewhat soft alloy, while more than 30 per cent. of zinc gives one which is less ductile. A somewhat commoner brass is composed of 66 per cent. of copper and 33 per cent. of zinc. Brasses containing more than 62 per cent. of copper are workable cold, but cannot be rolled hot.

The ordinary method of ascertaining the quality of brass locomotive tubes consists in ascertaining their composition by analysis, and submitting them to the mechanical tests of flanging the end and of hammering them flat, and bending double the sheets thus produced; this should be effected without the formation of cracks. The tensile strength of brass castings is 11 tons per square inch, and of rolled sheet 16 tons per square inch. The specific gravity of brass containing 66 per cent. Cu and 33 per cent. Zn is 8·3. Brass of good quality is made from the purest copper and zinc that can be obtained, and contains no metal (save in traces) other than copper, zinc, and lead, the last-named being present to the extent of less than 0·5 per cent. More than traces—*e.g.*, 0·05 per cent.—of arsenic are considered objectionable.

A special variety of brass used for sheathing ships is Muntz or yellow metal, containing 60 per cent. of copper and 40 per cent. of zinc; its specific gravity is 8·2. Since the copper in yellow metal falls below the limit given above for brass (62 per cent.), this alloy can be rolled hot. Its advantage for sheathing depends upon the fact that it is less corrodible than copper.

Gun metal is the name applied to alloys of copper and tin ranging from 91 per cent. Cu and 9 per cent. Sn to 84 per cent. Cu and 16 per cent. Sn. A grade frequently used contains 87·5 per cent. Cu and 12·5 per cent. Sn. Small quantities (up to 2 per cent.) of lead and zinc are often added. Gun metal is stronger than cast brass, having a tensile strength of 15 to 20 tons per square inch, and a compressive strength of about 50 tons per square inch. The 9 : 1 alloy has a specific gravity of 8·5. It is used for strong castings (being stronger than cast iron) for the more delicate parts of machinery, for cocks and the like where it is exposed to corrosion, and for bearings. In casting gun metal there is a great tendency to segregation, especially when the casting is massive, and cools slowly. Nearly white crystals that have thus separated may be seen in the fracture of slowly cooled gun metal. *Phosphor-bronze* is a gun metal containing lead and phosphorus, the following being a typical com-

position :—Cu, 79·7 per cent.; Sn, 10·0 per cent.; Pb, 9·5 per cent.; P, 0·8 per cent. It is used for bearings, pump linings, and other wearing parts. Many special bronzes are used for bearings. Such bearings are all called "brasses" in engineering parlance, whatever their composition; brass itself is, however, not well suited for bearings. A typical locomotive "brass" bearing, adopted after much experiment on a large American railway, contains—Cu, 76·8 per cent.; Sn, 8·0 per cent.; Pb, 15·0 per cent.; P, 0·2 per cent. The presence of the large quantity of lead is found to diminish the wear of the metal and the local heating of the journals.

Delta and Bull Metal.—Of late years brasses and bronzes have been made which are capable of being forged and rolled, and serve to replace ingot iron and mild steel for certain purposes where a strong metal not easily corroded is required. One use to which they have been recently put is the manufacture of ships' propellers. Delta metal is a ferruginous brass containing about 55 per cent. Cu, 43 per cent. Zn, 1 per cent. Fe, and traces of lead and phosphorus. Bull metal is an alloy of the same type. Both metals may be forged and rolled. When intended for such treatment, the ingot or bar to be worked is cast in a chill, so as to prevent segregation. Metals of this class have a tensile strength of about 18 tons per square inch when cast, and one of about 30 tons when rolled, with an elongation of 15 to 20 per cent. on 10 inches.

Aluminium bronze is an alloy of copper and aluminium containing up to 10 per cent. of the latter metal. It can be cast, forged, and rolled, and may replace mild steel for purposes where corrosion is to be resisted and its cost is not prohibitory. It has a high tensile strength. Thus, a 10 per cent. alloy (cast) has an ultimate tensile strength of about 40 tons per square inch, and the same metal when rolled an equally high tensile strength and an elongation of 30 per cent. Five per cent. aluminium bronze is well suited for the ignition tubes of gas engines. Aluminium brass castings containing 63 per cent. Cu, 33·3 per cent. Zn, 3·3 per cent. Al, 0·33 per cent. Si, were found to have a tensile strength of 31·4 tons, and an elongation of 0·4 per cent. A similar alloy rolled had a tensile strength of 37·8 tons, and an elongation of 9·7 per cent. Two per cent. aluminium brass can be used as ship's sheathing. In making aluminium bronze, repeated fusion and casting are necessary to obtain a homogeneous alloy.

White Bearing Metals.—Besides the bronzes mentioned above as being used for bearing metals, many "white metals" are made, consisting of alloys of lead, tin, antimony, zinc, and copper. Such mixtures are readily fusible, and are cast in the space round the journal to be supported. They are also used for lining "brasses" that have become worn. Thus, a

form of **Babbitt's metal** has the composition—Pb, 40 per cent.; Sn, 45·5 per cent.; Sb, 13 per cent.; Cu, 1·5 per cent. That used on the London and North-Western Railway has the composition—Sn, 84·2 per cent.; Sb, 10·5 per cent.; Cu, 5·3 per cent. Another now largely employed contains—Pb, 80 per cent.; Sb, 15 per cent.; Sn, 5 per cent. Alloys of this class, though of no great tensile strength, are sufficiently strong in compression to carry the load of even a heavy bearing; their comparative plasticity renders them less liable than "brass" bearings to "seize" and heat, and the coefficient of friction is generally low.

ALUMINIUM is at present but little used as a true structural material, though its employment in this direction is increasing. The commercially pure metal (99 per cent. Al) is white, not very lustrous, and easily dulled by exposure to air; the corrosion is, however, only superficial. When cast it has a tensile strength of 7 to 9 tons per square inch, with an extension on 4 inches of 15 to 20 per cent., though many specimens have a much smaller extension. After rolling, its tensile strength is increased to about 16 tons, with an extension of about 4 per cent. on a length of 4 inches. It is best worked warm, at about the temperature used for zinc. It is difficult to solder, and this property hinders its use for many purposes. The chief impurities of commercial aluminium are iron and silicon. The first is said to be injurious, but the effect of silicon is rather to increase the tensile strength, while diminishing the elongation. Alloys of aluminium containing a small quantity of copper, silver, nickel, or titanium have a higher tensile strength than the pure metal. Thus the addition of 2 per cent. of copper raises the strength of rolled aluminium to 19·5 tons; alloys containing 2 to 3 per cent. of titanium have a tensile strength of 18 to 27 tons per square inch in forgings, and similar results have been obtained with nickel and zinc. On account of its lightness and good electrical conductivity (about 59 per cent. of that of copper), it has been proposed to use aluminium for telegraph and telephone wires; and a wire with a copper sheathing and aluminium core, having a conductivity of 69 per cent. of that of copper, has also been devised.

NICKEL is used alone as a structural material to a trifling extent, its employment being practically confined to making culinary utensils and chemical apparatus. Its chief alloys are dealt with under *Nickel* in the section on *Metallurgy*. It finds a large application in the manufacture of nickel steel used for armour plates and guns. Such steel contains 3 to 5 per cent. of nickel (p. 19). A remarkable alloy of iron and nickel containing 25 per cent. of nickel has, when annealed (being then in its non-magnetic condition), a tensile strength of about 50 tons per square inch, and an extension of about 30 per cent.; when

strongly cooled it becomes magnetic, and then has a tensile strength of 85 tons, with an extension of 7 per cent. The foregoing tests were on wire. The metal in rod or plate, containing 25 per cent. Ni, 0·27 per cent. C, and 0·85 per cent. Mn, had a tensile strength (in the uncooled state) of 45·8 tons per square inch, with an elastic limit of 12·75, an extension on 8 inches of 29 per cent., and a reduction of area of 28·6 per cent.

ROOFING MATERIALS.

The chief roofing materials in common use are slates, tiles, sheet lead, sheet zinc, zinced ("galvanised") iron, and tinned iron (tin-plate).

SLATE is an argillaceous rock which is of sedimentary origin, and has had cleavage planes developed in it, its peculiar fissile character (slaty cleavage) being due to a re-arrangement of the particles of the rock consequent on compression. Slate generally consists essentially of aluminium silicate, coloured with ferrous oxide. Light coloured slates are sometimes found; dead black slates are rare. Iron sulphide is often present both as pyrites and marcasite. The former is not injurious, but the latter causes disintegration of the slate on account of the ease with which it is oxidised by weathering. Calcareous slates containing as much as 49 per cent. of calcium carbonate are also found. A slate of good quality should have a fine grain, should ring sharply when struck, and should not be easily scratched by the finger nail. Its colour does not serve as a criterion of quality. The most important property, besides toughness, to be considered in judging slate, is its degree of porosity. It should be as nearly non-absorbent as possible. The variation of slates in this respect is shown by the fact that the volume of the pores of the slate varies from 0·05 to 6 per cent. of the apparent volume of the whole slate. Many commercial varieties of slate are distinguished. The Welsh are considered the best, and of these the Silurian are better than the Cambrian slates, for they are less siliceous than the latter, and more easily cleaved. The sizes most in use for roofing are distinguished by fancy names—*e.g.*, "wide viscountesses," "small ladies," &c., the enumeration of which cannot be attempted here.

Certain calcareous sandstones—*e.g.*, **Stonesfield slates,** which are not true slates, are used for ornamental roofing, but, being comparatively thick, their weight is against their general employment. Slate is an excellent roofing material, but is somewhat costly, and on account of its usually dark colour absorbs much heat when exposed to the direct rays of the sun, thus failing to keep the building beneath cool.

TILES are made by moulding and burning brick clay; their

manufacture is described in the chapter on *Clay Industries*, Vol. II. They are thicker, heavier, and more porous than slates. For tiles to be efficient they must fulfil one of two conditions. Either they must be of open porous structure, so that water soaking in may be able on freezing to expand without splitting the tile, or they must be burnt at a clinkering temperature, and be as dense and non-porous as stoneware or biscuit porcelain (*q.v.*), so that water cannot find its way in. The same end may be attained by soaking porous tiles in tar. Glazed tiles with a porous body are of little use, as the least imperfection in the glaze permits the entrance of water, which in expanding by freezing in cold weather causes the glaze to scale off. Dense clinkered tiles can be glazed without this result, but in this case the glaze is of small utility save as giving a smooth surface upon which lichens cannot grow.

ZINCED IRON (*galvanised iron*) is largely used as a roofing material, and also for the entire construction of sheds and other cheap and temporary structures. The process of "galvanising" consists in removing the scale from the plates and other articles (a preliminary annealing being performed in the case of plates) by pickling in hydrochloric acid, washing, scouring with sand, and passing through a bath of melted zinc which is covered with ammonium chloride. The latter serves as a flux, and induces the coating of the iron by the zinc. For galvanised sheet, a little tin (2 to 3 per cent.) is added to the bath, and produces large crystalline spangles on the finished goods, which appearance is often erroneously taken as a proof of good quality. A small quantity of aluminium—about 0·01 per cent.—is often added to the zinc bath to reduce any zinc oxide that may be diffused through the metal. The plates are generally brought out between rollers or brushes to economise zinc, the proportion of which adhering to the iron is usually reckoned in ounces per square foot, 2 ounces being a good average coating. Zinced sheet is often corrugated to increase its strength and prevent it from buckling when used for walls and roofs. A considerable proportion of iron passes into the galvanising bath and sinks to the bottom as a zinc-iron alloy. This hard zinc, containing about 5 per cent. of iron, is removed and liquated from time to time. As the iron of the tank is also dissolved by the zinc—resulting in the ultimate destruction of the tank—attempts have been made to avoid contact of the zinc with the tank by allowing the zinc to float on a layer of melted lead (to protect the bottom), and by lining the sides of the tank with fire brick. The acid pickling bath used to clean the plates, &c., may not legally be turned into sewers or rivers, and is apt to become a nuisance. It contains about 10 per cent. of iron as ferrous chloride, and but little free acid. An attempt at its utilisation has been made by Turner, who allows the liquor to trickle into a furnace, where the liquid evaporates and the

ferrous chloride is decomposed in accordance with the equation $2FeCl_2 + 2H_2O + O = Fe_2O_3 + 4HCl$. The hydrochloric acid is condensed by the usual means (see *Salt-cake*, Vol. II.), and re-used. The ferric oxide serves as fettling in puddling furnaces. Most grades of cast iron, wrought iron, ingot iron, and steel, and articles of the most diverse shape may be zinced, but certain differences in facility are observed. Thus cast iron is least easy to zinc; wrought iron, ingot iron, and mild steel take the metal readily; but hard steel—*e.g.*, wire for ropes—is less readily coated. The high temperature of the galvanising bath (420° C. = 788° F.) also affects the temper of hard steel wire, diminishing its tensile strength. The fact that zinc forms an alloy of low strength on the surface of the iron, immediately beneath the visible coating, appreciably impairs the strength of goods of light section—*e.g.*, wire and small chains. Iron is sometimes coated with lead instead of zinc. The general method of procedure is the same, but even greater care must be bestowed on the preparation and cleaning of the iron to be leaded, as lead adheres less readily than zinc. The cheapness of lead (£12 per ton, as compared with £22 per ton for zinc*) gives it an advantage, as does its indifference to acids and its ductility, which prevents it from tending to scale when the article coated with it is bent. It does not impair the strength of the iron or steel to which it is applied, and the risk of softening hard steel wire (referred to above in the case of zinc) is much lessened, as the fusing point of lead is only 325° C. = 617° F. Against these properties must be set the inferiority of its protective action to that of zinc (*v.i.*), and its toxic qualities, which make it unsuitable for lining cisterns and pipes which are used for holding and conveying water. If used in the same thicknesses as zinc, it increases the weight of the coated article, on account of the difference between the specific gravity of lead (11·4) and that of zinc (6·9). The advantage in point of cost mentioned above is therefore less than appears from the comparison of the prices per ton of the two metals.

TINNED IRON (*tin plate*) is not much used as a structural material (save occasionally for roofs, for which it is ill adapted), but is conveniently considered here on account of its analogies to and differences from zinced plate. It is used for small hollow ware, and inasmuch as it can be cheaply soldered and made up, it is not ousted by zinced iron in spite of the low price of zinc compared with that of tin. The process of manufacture is as follows:—Heated bars of wrought iron or ingot iron are rolled to a plate, which is folded across the middle, again heated and rolled. The doubling and rolling are repeated until as many as thirty-two thicknesses have been rolled. The edges of this compound plate are sheared off, and the individual plates split asunder. The coating of iron scale which forms during the rolling prevents the plates

* Prices of all metals fluctuate considerably.

from welding together. The plates are then pickled in dilute sulphuric acid,* scoured, and annealed. The surface is then improved by cold rolling, which renders a second annealing necessary. After a second pickling in a more dilute acid, the plates are passed into the "grease-pot," containing melted tallow or palm oil. They are then dipped in the tin bath, the metal in which is covered, to prevent oxidation, with grease or zinc chloride. To perfect the coating of tin, passage through several successive tin pots follows. By this systematic working, the preliminary coating is done by the most impure bath, and the final layer put on in a pot of nearly pure tin. To squeeze off the excess of tin, the plate is finally passed through rollers running in a grease bath. Although tin plate has a layer of tin-iron alloy intermediate between the iron plate and the tin coating proper, yet the diminution in strength due to this layer is less marked than in the case of zinced iron (p. 27). Thus it happens that thinner plate and wire can be tinned than can be zinced without injury.

STRENGTH, PERMANENCY, AND PRESERVATION OF MATERIALS.

STRENGTH OF STRUCTURAL MATERIALS.— In the preceding sections the strength of ordinary metals used in

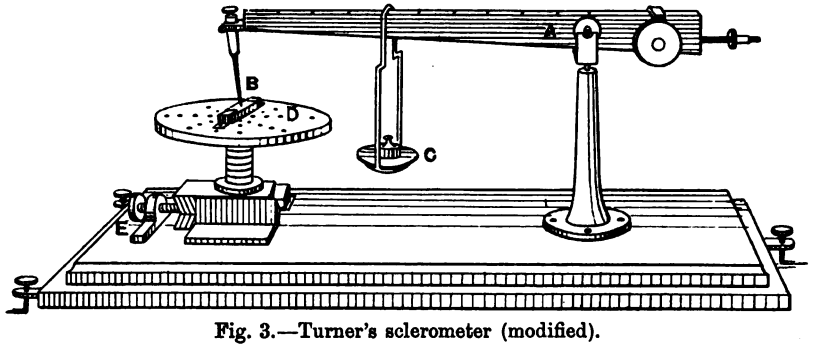


Fig. 3.—Turner's sclerometer (modified).

A, Steelyard beam; B, diamond pointed style; C, scale pan; D, rising table; E, screw.

construction has been incidentally given as a criterion of their quality. In the appended tables their values are compared with the corresponding figures for other materials. In general the

* Pickling any light iron article in acid so as to cause the evolution of hydrogen at its surface renders it brittle by absorption of hydrogen; this brittleness is removed on heating.

mechanical property, the possession of which causes the choice of the material for its ordinary functions, is given, sometimes to the exclusion of its other less important mechanical properties.

The following figures refer to the mechanical properties of metals at the ordinary temperature—*e.g.*, at 15° C. = 59° F. At higher temperatures—*e.g.*, 300° to 400° F. (= 149° to 204° C.)—their tensile strength is generally greatly reduced, a matter of much importance in structures carrying heavy loads at high temperatures, such as steam boilers. But few exact data dealing with this matter have been published.

STONE, BRICK, CONCRETE, AND CEMENT.

Name.	Compressive Strength. Tons per Square Foot.	Tensile Strength. Lbs. per Square Inch.	Weight per Cubic Foot. Lbs.	Percentage of Water absorbed. Reckoned on Weight of Stone.
STONE—Sandstones—				
Prudham, . . .	455·3	...	142·5	4·00
Craigleith, . . .	352·8	453	...	3·2
Granites—				
Rubislaw (Aberdeen),* .	1098·8	...	163·7	0·09
Kenmay (Aberdeen),† .	1211·1	...	161·0	0·21
Whinstone, . . .	769·0	1469	170·0	0·10
Calcareous Stones—				
Oolitic limestone (Portland)	287·0	...	137·6	6·84
Dolomitic ,, (Anston),‡	301·9	...	132·2	7·50
True dolomite, . .	577·4	...	145·4	4·62
Marble (White Italian),	1400	722	170	Trace.
Marble (Red Devon), .	476·6	...	...	...
BRICK—				
London stock, . .	128	...	...	...
Gault brick, . . .	135·4	...	...	19
Staffordshire blue brick,	267·8	...	...	3·7
Red brick (machine made),	113·8	...	...	9·9
CONCRETE—				
1 cement : 6 ballast (twelve months old), . .	91	...	...	...
1 cement : 2 ballast, .	160	...	...	...
CEMENT—				
Neat (seven days old), .	2714	400	...	...
1 cement : 3 sand (twenty-eight days old), . .	1074	180	...	...

* Used for London Bridge. † Used for Forth Bridge.
‡ Houses of Parliament.

METALS.

Name.	Tensile Strength. Tons per Square Inch.	Elastic Limit.	Extension. Per Cent.	Reduction of Area. Per Cent.
Cast iron,	7	2	Inappreciable	Inappreciable
Malleable cast iron,	17·8	...	5·6	6·9
Wrought iron,	22–25	13–15	26	30–40
Ingot iron (0·1 per cent. C.),	25	15	28	50
,, (0·2 ,, ,,),	28	17	24	40
,, (0·3 ,, ,,),	35	21	20	30
,, (0·4 ,, ,,),	40	24	15	25
Cast steel, hard (0·6 per cent. C.),	60	...	1	...
Hard steel wire (fine gauge),	100	...	1	...
Copper (tough pitch),	13–15	6–8	40	40
Brass (2 copper : 1 zinc),	15	...	...	...
Gun metal (9 Cu : 1 Sn),	15–20	...	...	...
Phosphor-bronze, rolled,	32	Occasionally none. Sometimes 24 or higher.	18	50
,, ,, cast,	18	12	11	10
Muntz metal,	22	...	...	...
Delta metal, cast,	32	16	18	20
,, ,, rolled,	45	20	20	22
Bull metal, rolled,	36	21	10	15
,, ,, cast,	24	16	10	15
Manganese bronze, cast,	30	15	28	20
Aluminium bronze (10 per cent.), rolled,	40	...	30	...
Aluminium, cast,	5	2–5	3	5
,, rolled,	16	...	4	...
Nickel,	85	...	...	...
Zinc, sheet,	7	...	...	...
Lead,	1	...	...	...

The resistance of materials to wear (abrasion or attrition) depends jointly on their tenacity and hardness. The latter property may be best ascertained by the use of Turner's sclerometer (hardness measurer), a modified form of which, devised by one of the authors, is shown in the figure on p. 28 (Fig. 3). A steelyard beam, A, swings on a pivot in a horizontal plane, and oscillates on knife edges in a vertical plane. At the end remote from the knife edges is a style, B, shod with a diamond point. This style is set at an angle with the plane of the beam for a purpose which will be explained later. A scale pan, C, slides along the beam, which is graduated, and by its means a load varying from 1 to 100 grammes can be placed upon the diamond point. The piece to be tested is prepared with a polished surface free from scratches, and is clamped on the rising table, D. The diamond point is loaded with a known pressure and drawn across the polished surface. The style carrying it is

sloped, as mentioned above, to prevent "chatter." By means of the screw, E, the table is moved bodily a short distance—*e.g.*, $\frac{1}{50}$ inch—and another trial made with a different load. The load which just suffices to abrade the surface of the specimen is a measure of its hardness. The instrument is preferably used in conjunction with a low-power microscope (1 inch objective) to view the scratches and decide which corresponds with the abrading load. The following table (*Turner*) shows the hardness of various materials, the figures being the load in grammes required to just scratch the specimen when tested by the sclerometer:—

Steatite,	1
Lead (coml.),	1
Tin ,,	2·5
Rock salt,	4
Zinc (annealed),	6
Copper ,,	8
Calcite,	12
Softest iron,	15
Fluor spar,	19
Mild steel,	21
Tyre ,,	20-24
Apatite,	34
Hard cast scrap,	36
Window glass,	60
Hardest chilled iron,	72

In choosing a material of construction in respect of its strength as distinct from its durability, it may be said that where static compressive loads have to be borne a rigid material, such as stone, concrete, or such metals as are hard, and have a high compressive strength in the cast state (*e.g.*, cast iron and gun metal), is preferable. When dynamic stresses have to be resisted, and toughness as distinct from rigidity is a necessity, some form of wrought metal, such as wrought iron, ingot iron, copper, brass, and special copper alloys (*e.g.*, phosphor-bronze), is employed. The tendency of most cast metals, if allowed to cool slowly, is to assume a crystalline structure favourable to rigidity and compressive strength rather than to toughness and tensile strength. By working—*e.g.*, rolling or forging—the crystals are commonly deformed into longitudinal fibres, and the metal acquires a higher tensile strength and ductility, with some loss of rigidity. Thus, as mentioned under iron, the cast metal is used for bed plates and standards, and wrought or ingot iron for moving parts. The use of ingot iron or mild steel for rails is no exception to the rule, as the stresses to which a rail is subjected are eminently dynamic.

PERMANENCY OF STRUCTURAL MATERIALS.—The permanency of building materials depends jointly on their inherent powers of resisting the destructive agents to which they may be exposed, and on the character of their environment, which may aid or hinder the disintegrating and corroding effect

of such destructive agents. These destructive agents may be divided into two classes, mechanical and chemical, the former being the more important.

Under the first head are included such influences as erosion by sand mechanically driven against the building by the wind, and the attack of rain and frost. With regard to the effect of sand it is obvious that it is likely to occur in places where the soil is loose and siliceous and the wind often high. Thus buildings on the sea coast are especially liable to this form of attack, and the side of a given building facing the quarter from which the prevailing wind blows, naturally suffers most. The effect of rain and frost is similarly localised by the action of the prevailing wind. The wind forces the rain into the stone, but, at the same time, causes the evaporation of the moisture when the rain has ceased; this will not, however, compensate for the increase of the action of acids which may have been carried in by the rain (see *Chemical corrosive agents*). Thus it comes about that the most exposed side of a building suffers most from weathering. Probably the greatest mechanical effect is brought about by frost, which tends to disintegrate the stone by the expansion, in the act of freezing, of the water enclosed in the pores, with consequent separation of particles of the stone. Mere cold, if the stone be dry, has no deleterious effect, whence it follows that stone as quarried and containing much moisture must be rendered fit for building purposes by being "seasoned," *i.e.*, allowed to dry. The amount of water which a stone will absorb under its conditions of use depends on its texture, a loose, porous structure causing a large absorption. Even where the new stone does not absorb much water, it may tend to do so after use, if the grains composing it be easily removed by the mechanical action of wind referred to above, and its superficial structure thus rendered more porous. The capability of the stone to resist the action of frost is ascertained by a direct freezing test. The test piece is saturated with water and alternately frozen and thawed (a dozen times or more), and the loss of weight of the block by exfoliation determined. A test formerly much in vogue (Brard's test), which consists in soaking the stone in a saturated solution of sodium sulphate, allowing the salt to crystallise in its pores, and repeating the operation, is fallacious, as the solution of sodium sulphate contracts in solidifying, and the expansion of water in the act of freezing is not imitated. The determination of the maximum amount of water which a stone will absorb is effected by soaking a test piece of known dimensions and weight until it is saturated, and ascertaining the increase of weight caused by the water which it has taken up. In the case of slate similarly tested, diphenylamine (M.P. 54° C. = 129° F., B.P. 310° C. = 590° F.) has been recommended. The behaviour of different classes of stones (and of

bricks) with regard to the action of frost, may be thus generalised :—

(1) Those which are impermeable to moisture must plainly be unaffected. Such are stones of extremely close structure—*e.g.*, granite, and bricks and tiles burnt at a clinkering temperature.

(2) Those which are porous but are of open texture and fair cohesion are likely to suffer little, as although water finds its way into them, yet there is room for it to expand on freezing without causing disintegration.

(3) Those which are not very porous but are still hygroscopic, such as certain argillaceous varieties, are liable to serious attack, as water finds its way in and freezes in the pores without having room to expand.

The only satisfactory manner of determining the frost-resisting power of a stone is to submit it to the freezing test above-mentioned.

Although the foregoing paragraphs have dealt chiefly with the behaviour of stone, they apply equally to artificial stone, including brick and concrete. The latter have, however, certain defects of their own. Thus, bricks which have been made from clay containing alkali salts are liable to efflorescence, the salts (sodium sulphate and carbonate) appearing on the surface of the brick with a disfiguring effect. Other causes of the presence of soluble salts inducing efflorescence, are the presence of iron pyrites in the clay, and of sulphur in the fuel used to burn the bricks; both these give rise to sulphuric acid during the burning, and the alkalies and alkaline earths present in the clay are converted into sulphates. Pyritic clay should, therefore, be avoided. Similar efflorescence occurs with artificial stone which has been made by a process involving the use of an alkaline silicate, as any residual alkali left after the washing process which the stones undergo, is gradually converted into carbonate, and appears upon the surface. Concrete and cement mortar may also give efflorescences of calcium hydroxide and carbonate, and, if in contact with sea water, may develop growths composed chiefly of magnesium hydroxide, due to the interaction of the magnesium salts of the sea-water and the lime compounds of the concrete. The foregoing efflorescences are sometimes fairly harmless; frequently, however, they tend to cause damp places on the structure, destructive of paint and plaster, and even leading to the detachment of fragments of the wall. In the case of concrete these efflorescences owe their injurious character to the chemical actions involved rather than to any mechanical effect which they exert. They will be dealt with more fully in the next section.

The growth of lichens on stone and brick influences the permanency of these materials in a manner depending on the

prevailing conditions. Thus, such a growth may serve as a protection from rain, but, on the other hand, may prevent the surface from drying. Since the plant needs a foothold, a smooth surface will be less able to afford support than a rough one. Porous brick and tile are typical materials upon which such growths occur.

In the case of metals, the possibility of mechanical destruction is less imminent than with stone and brick, on account of their closeness of grain and the fact that they are less frequently used than stone or brick for outside work, or if so used are protected by some external envelope. There is, however, one cause of failure (previously adverted to incidentally) which must not be overlooked in designing and maintaining metallic structures. It has been found that the frequent application of a load, well below that which the metal if tested in the ordinary way is found to be easily capable of bearing, eventually produces "fatigue" in the metal, tending to change its structure and causing it to become crystalline and brittle. It may be supposed that repeated agitation allows the molecules of the metal to assume the positions corresponding with the form in which it crystallises, and the consequent alteration of a fibrous to a less interlocking structure naturally decreases the strength of the material. Instances of the change in question are afforded by the failure of railway axles, which have been found to become crystalline after long use, and by the sudden snapping of brass chains, such as are used to support gas pendants, and are therefore subjected to repeated strains from the oscillation of the burners depending from them.

The use of many structural materials involves operations which have a considerable effect upon the permanency of the structure. This influence is distinct from that exerted by the quality of the materials of construction themselves. All methods of uniting separate pieces of the same material, or of one material with another, come into this category and may be considered here.

The best method of joining is that of **autogenous soldering**—*i.e.*, the union of two pieces of the same material by bringing together the parts to be joined in a liquid or semi-liquid state. The process known *par excellence* as autogenous soldering is **lead-burning** (see *Vitriol*, Vol. II.). The operation of lead-burning consists in applying two clean surfaces of lead to each other and fusing their opposing edges, so that the molten metal forms a seam between the two, absolutely continuous and homogeneous with the portions joined. Fusion is effected by the flame of a blowpipe fed with hydrogen and air, the source of heat being sufficiently intense to fuse the metal locally without heating the adjacent portions, and being also clean and free from products of combustion (*e.g.*, sulphurous gases) capable of tarnishing the

metal to be joined.* Another case of strictly autogenous soldering is afforded by the **welding** of iron and of steel. Here the metal is not actually fused so that it will intermix by its own flow, but when in a plastic state it is caused to flow by pressure, applied either as a steady stress or by hammering. The simplest form of welding is that practised by the smith, and consists in raising the temperature of the parts to be welded to a "welding heat"—*i.e.*, nearly the highest temperature of the forge (see *Industrial Temperatures*, p. 83), cleaning the surface by slagging (*fluxing*) off the oxide with sand or borax (which thus serves as a *flux*), and hammering together the surfaces to be joined. Wrought iron will stand a high welding temperature, and is correspondingly easy to weld. Ingot iron and mild steel are somewhat less easy to weld, and are worked at a rather lower temperature; higher carbon steel needs a still lower temperature and more careful working, borax and sal-ammoniac being used as fluxes, as a slag formed by the aid of sand is not sufficiently fusible at a red heat. A neat application of the use of a flux to be placed between the surfaces to be welded has been recently devised, and consists in employing fine soft iron-wire gauze, the meshes of which are filled with borax glass (fused borax). Pieces of this are placed between the metal to be welded, and present the flux at the precise spot where it is needed. The difficulty of welding high carbon steel is increased when it has to be welded to ingot iron or wrought iron, as a temperature suitable for the former is too low for the satisfactory working of the latter. Certain tools—*e.g.*, hack-saws, vices, and hammers that need a hard working face and a soft, tough backing —are produced by welding hard steel to softer steel or iron. A skate blade and a compound armour plate are examples of the same practice. Iron is the only structural metal which can be united by ordinary welding, platinum alone sharing this property. A recent method of welding which has found considerable employment is that depending on the use of electricity as a source of intense and local heat. A current of large quantity and low pressure, obtained from an ordinary dynamo by the interposition of a step-down transformer,† is passed through the bars (or other pieces of iron) to be welded. At the point where they touch, the resistance caused by their imperfect contact causes the transformation of electrical energy into heat; as heating proceeds the resistance rises, in accordance with the general behaviour of metallic conductors, and more heat is generated, the opposed

* The strength and permanence of concrete made *in situ* and built up to form what is in essence a monolith, are largely due to the method of jointing, which is quite comparable with autogenous soldering.

† A transformer is the modern equivalent of an induction coil: a step-up transformer is essentially an induction coil; a step-down transformer a reversed induction coil.

ends of the bars quickly reaching a welding temperature. During the process they are pressed together in the direction of their length, and the joint is finished by hammering in the usual way. An alternative method, applicable when it is not possible to make the two pieces of metal to be joined act as both electrodes, consists in the use of one as an electrode, and a carbon rod as the other electrode, local heating by means of the arc thus produced being engendered, and welding of the two pieces of metal effected. This method has also been applied to lead-burning. Electric brazing is also practised. The chief advantages of electrical welding are its rapidity and cleanliness, and the ease with which massive pieces of metal may be welded when already in place. Probably on account of the extremely local heating of the welded joint, an electrical weld is not as tough and reliable as a good hand weld, which can, when made in wrought iron, be bent through an angle of 180° cold, whereas an electrical weld usually fails at about 135°. Electrical welding, on account of the high and local temperature at command, can be applied to other metals than iron. Copper can be welded to copper, aluminium to aluminium, and indeed most metals to themselves and to each other. In these cases the joint is made by local fusion rather than by welding in the ordinary sense. Autogenous soldering, using the phrase in its widest sense, has the advantage over other methods of joining that risk of destruction by the formation of galvanic couples from the contact of different metals with each other is minimised.

Methods of **soldering,** as distinct from autogenous soldering, consist in joining two metals by an alloy more fusible than either, but capable of forming an alloy with each. **Hard soldering** or **brazing** is used chiefly for copper and brass, the fusible alloy employed being a brass rich in zinc; the ordinary **hard solder,** "spelter,"* for brass consisting of 1 part of copper and 1 of zinc, that for copper (and iron) having the composition of 2 of zinc to from 3 to 6 of copper. The melting point of the solder is of course chosen so as to fall below that of the metal to be soldered. This difference in melting point is indicated by the terms hard and soft spelter, the former being the less fusible. The flux used is borax, which is generally mixed with the solder, the latter being in the form of filings or wire. The mixture is made into a paste with water and applied to the joint, which is wired or pinned together so that it may not shift during soldering. The heating is effected by a coke fire or a gas blowpipe. The action of borax as a flux is due to its power of dissolving metallic oxides, while leaving metals unattacked; cleaned metallic surfaces are thus presented to the action of the solder, a condition essential to the formation of alloys. **Silver solder** is another

* Spelter is used technically to mean (1) hard solder for brazing, and (2) cast zinc, as opposed to rolled or sheet zinc.

hard solder used for fine work in the same way and with the same flux as spelter. Hard silver solder contains 1 part of copper and 4 of silver, a softer variety containing 1 of copper and 2 of silver.

Soft solder is used for joining tin-plate and the more fusible metals and alloys—*e.g.*, zinc, lead, tin, and pewter. It is also largely used for brass and copper where strength of joint is not essential and the low fusing point of the solder is no detriment. Most varieties of soft solder are lead-tin alloys. **Fine solder,** the most fusible of common solders, contains 2 of tin to 1 of lead; **tinman's solder,** 1 of tin to 1 of lead; **common plumber's solder,** 1 of tin to 2 of lead; **coarse solder,** 1 of tin to 3 of lead; **pewterer's solder** consists of 2 of tin, 1 of lead, and 1 of bismuth, the object of the addition of the latter being to lower the fusion point below that of the pewter. Various fluxes are used, according to the nature of the metal to be soldered. Iron, which is less frequently soldered than the metals enumerated above, requires sal-ammoniac as a flux; for tin-plate, chloride of zinc solution or rosin is employed; for copper, any one of the three can be used; hydrochloric acid or zinc chloride is used for zinc; tallow for lead —*e.g.*, in "wiping" joints; and olive oil for pewter. Two classes of fluxes may be distinguished in this list. The first has a purely protective action, preventing the oxidation of the previously-cleaned metal surfaces; examples of this class are rosin, tallow, and olive oil. The second has a cleansing action, any oxide-film on the metal being fluxed and removed; sal-ammoniac, zinc chloride, and hydrochloric acid are cases in point. The use of these latter depends on the volatility and fusibility of most metallic chlorides. The choice of a flux depends mainly on the fusibility of the metal to be soldered, and on the readiness with which it oxidises. Thus tin (or tin plate), which does not easily oxidise and fuses readily, needs a fusible solder and a fusible flux which may be merely protective and have no cleansing action; such a flux is rosin. Copper is fairly non-oxidisable as compared with zinc or iron, and may be soldered with rosin, but zinc chloride is generally used. Zinc is a difficult metal to solder, as it is easily oxidisable and needs a cleansing flux. When hydrochloric acid is used, zinc chloride is formed *in situ*, but the zinc chloride can be also applied as such to the surface. In both cases zinc oxide is dissolved and a clean surface presented to the solder. The technical name for zinc chloride solution is "killed spirits of salt," it being made by "killing" spirits of salt (hydrochloric acid) by the addition of scrap zinc until saturation is reached. The soldering of iron and of copper is much facilitated by previous tinning, the process consisting in wetting the clean surface with pure tin before the soldering proper is performed.

A method of joining iron pipes where the joint will not need to be broken after it has been once made, consists in the use of a

"rust-joint." The cement for this joint is made by mixing iron borings or filings (80 parts) with sal-ammoniac (1 part) and sulphur (2 parts), the whole being moistened with water and rammed into the joint. The joint is essentially iron rust, rapid rusting being induced by the minor ingredients.

Passing from mechanical causes of permanency or its opposite, **chemical agents** influencing the permanency of structural materials must be considered. The chemical agents which lead to the destruction of building materials are **water,** acting as a solvent and hydrating agent, **carbon dioxide,** and **sulphurous and sulphuric acids,** the last three acting simply as acid solvents in the presence of water. Nearly the only structural material suffering simple solution is plaster of Paris (calcium sulphate), including Keene's cement (*q.v.*, Vol. II.). On account of its solubility it is only used for work protected from the weather, or for temporary facing of hydraulic mortar exposed to the action of water, in order that the mortar may be protected while setting; the plaster is ultimately washed away, having fulfilled its function. The concrete itself, even when fully set, is not necessarily permanent when its structure is porous and water has free access to it, as hydraulic cements are by no means perfectly insoluble in water. The presence in the water of salts with which the hydraulic cement is capable of reacting—*e.g.*, salts of magnesium—accelerates such change. Destruction may also be induced by the action of calcium sulphate in sea water brought into contact with hydraulic cement, inasmuch as this salt forms a definite compound with the calcium aluminate constituting an important part of the composition of the cement, and produces internal expansion or "blowing." As an hydrating agent, water will sometimes cause the disintegration of bricks which have been made from clay containing small lumps of chalk that have not been comminuted before the burning of the brick. The quicklime produced by the burning of these lumps expands in slaking, and splits off portions of the brick. When the chalk is thoroughly crushed and mixed, it is harmless, as on burning, stable acid silicates of lime are formed, which do not expand by slaking on exposure to water. Carbon dioxide, sulphurous acid, and sulphuric acid have but little effect on dry structural materials, but are actively corrosive in the presence of water. It follows that all important parts of buildings should be protected from moisture, or well drained. Sandstone and brick, being acid materials, are not much attacked by these acid gases. Calcareous stones, on the other hand, being basic in character, are much corroded. The attack of calcareous stones is particularly severe in towns, where the air is laden not only with carbon dioxide, but also with sulphurous and sulphuric acids from the combustion of fuel, coal always containing sulphur (*v.i.*). The action of CO_2 on calcareous stones is due to the solubility of the earthy car-

bonates—*e.g.*, $CaCO_3$ and $MgCO_3$—in water containing CO_2. The activity of such strongly acid substances as SO_2 and SO_3 needs no special explanation. The more porous a stone, other things being equal, the more readily will it be corroded. Thus in the case of granite, which is almost perfectly impervious, corrosion is extremely slow, although the finely-divided stone is fairly easily attacked. Another corroding agent is atmospheric oxygen, when an oxidisable material such as pyrites is present in the stone. Pyrites (particularly the form known as marcasite) in stone or slate is oxidised by air and moisture to sulphates of iron, and causes disintegration and corrosion.

The **corrosion of metals**, which are completely impervious, necessarily proceeds wholly from without, and is more essentially due to oxidation than to the direct solvent action of acids, although the latter enhance the severity of the attack. The decay of iron, commonly known as **rusting**, is especially rapid and far-reaching, on account of the fact that the oxidation of iron is both attended by the evolution of much heat and is easily initiated (*cf.* the oxidation of aluminium, *q.v.*), and also because the rust formed does not protect the rest of the iron, but rather increases its corrosion. It appears that the simultaneous presence of water, oxygen, and an acid (generally carbonic acid) is necessary for the rusting of iron. In the absence of any one of these, but little rusting occurs. Moreover, the presence of an alkali, or even an alkaline carbonate, prevents the rusting of iron. The rusting of iron may be viewed as taking place in two stages, according to the equations—

$$(1)\ Fe + H_2O + CO_2 = FeCO_3 + H_2$$
$$(2)\ 2FeCO_3 + 3H_2O + O = Fe_2(OH)_6 + 2CO_2$$

Taking this view of the change, it is apparent that a small amount of CO_2 may be instrumental in rusting an indefinitely large amount of iron. The elimination of hydrogen in the first stage of the reaction causes the removal of carbon (as hydrocarbons) from iron containing that element. It has been shown that rust is not pure hydrated ferric oxide, but contains hydrated ferrous oxide, the two being at least partially present as hydrated ferroso-ferric oxide, which accounts for the fact that common rust is attracted by a magnet. This intermediate state of oxidation may arise from the action of hydrated ferric oxide on iron, yielding hydrated ferrous oxide. This latter may in turn oxidise and act upon the remaining iron, the hydrated ferrous oxide serving in fact as a carrier of oxygen from the air to the iron. The rate of rusting of grey cast iron is generally slower than that of wrought iron or ingot iron. These two forms of the metal corrode the more rapidly with rising content of carbon, a generalisation which extends to cast steel and white cast iron containing much combined carbon.

Rust will generally contain its constituents in proportions exemplified below:—

	Per cent.
Moisture,	11·77
Siliceous matter,	3·33
Fe_2O_3,	66·82
FeO,	3·99
CaO,	0·76
MgO,	Trace.
CuO,	Trace.
Combined H_2O and loss,	13·33

Rusting is increased by **galvanic action** set up by contact of the iron with a metal electro-negative to it—*e.g.*, copper or tin. Thus, tin plate rusts more rapidly than unprotected plate at any spot from which the tin has been removed, the surrounding tin forming a galvanic couple with the exposed iron. The corrosion of iron railings, set at their foot in lead, which takes place very locally just above the point of contact of the two metals, is due largely to galvanic action. The same applies to iron protected by a film of copper rolled on or electrolytically deposited; the protection is satisfactory only as long as the coating is perfect. With zinced iron, on the other hand, slight imperfections of the coating are of less importance, as the zinc is electro-positive to iron and is the attacked metal of the couple, the exposed iron being protected at the expense of the zinc. This protection, though useful when the zinced iron is uniformly wetted, is not necessarily effective when the metal is only sprinkled with moisture, as a given spot of water may be exclusively in contact with the iron, and thus no couple may be formed. Zinced iron is not very resistant to salt water and sea air, the zinc being rapidly stripped by the action of chlorides, and the iron exposed. Two pieces of iron of different kinds may also form a galvanic couple, and increase the rate of rusting. Iron of all sorts is far from perfectly homogeneous, and this want of uniformity may lead to local rusting without contact with any other metal. Thus, wrought iron often contains slag unevenly distributed, and the loose porous places caused by the presence of the slag are good starting points for "pitting." Ingot iron may contain manganese disposed irregularly, and pitting may result from this circumstance.

This kind of corrosion is illustrated by the attack of propeller shafts at the point where they project from their brass sheathing; this has been found so serious as to necessitate special methods of protection.

Copper is less easily oxidised than iron. When exposed, however, to moist air, it is attacked, with the formation of basic carbonates of copper, a bluish-green film being formed. On account of the readiness with which copper is attacked by cupric salts—the cuprous salts formed serving as oxygen carriers—

progressive corrosion is to be expected. The presence of an acid gas enhances the corrosion and particularly increases its progressive character. If the acid gas be HCl, or if the copper be exposed to a solution of salt (in the presence of air), the corrosion is caused by the formation of an oxychloride instead of a basic carbonate. Although attacked by sea water, copper is less rapidly corroded by this agent than is iron, and on this account has been used for sheathing ships. The copper salts formed, moreover, constitute by their poisonous action a certain protection against fouling by marine growths. Copper for vessels for containing or conveying articles of food or drink are thickly **tinned** on the inside, the melted tin being wiped upon the cleaned surface of the copper in the presence of a flux, as in soldering. Where strength and resistance to accidental overheating are not essential, pure tin may be substituted for tinned copper with advantage. Silvered copper and pure silver are also used in special cases—*e.g.*, in the worms of acetic acid stills. The behaviour of most copper alloys —*e.g.*, brass—in respect of corrosion is similar to that of copper, but copper-tin alloys, as, for instance, bronze and gun metal, are less easily attacked than copper itself. Statuary and ornamental bronze gradually acquires by exposure a protective film, ranging in colour from green to nearly black, which is termed a "patina," and improves the appearance of the metal. An artificial patina may be produced by slightly corroding the surface of copper and its alloys by such saline solutions as ammonium chloride in conjunction with copper salts. Treatment of this kind comes under the general head of **metal colouring**; for details, special manuals must be consulted.

Copper aluminium alloys (aluminium bronzes) are remarkable for their resistance to corrosion, and on this account are used for ships' fittings, propeller blades, and filter press plates, where their cost is not excessive. The fact that aluminium alloys with copper with the occurrence of an exothermic reaction, doubtless contributes to the stability of the alloy.

Zinc oxidises superficially in moist air, but the coating of zinc oxide or basic carbonate produced affords sufficient protection for the underlying metal. When acid gases are present in the air, or when the metal is in contact with solutions of chlorides, the film dissolves and corrosion proceeds. Contact with an electro-negative metal or the solution of a salt of one—*e.g.*, copper —is particularly fatal to zinc, as a couple is formed, and then corrosion proceeds at a rate to be expected from the oxidisable character of zinc. Pure zinc is very difficult of attack; commercial zinc, containing lead, is more readily corroded, as it has within it the elements of a couple. Zinc, when used in the form of the coating on zinced iron, for pipes and cisterns, resists the action of calcareous, slightly alkaline waters well, a coating of basic carbonate protecting the metal. Soft waters containing

traces of organic acids and nitrates (which suffer reduction to ammonia), however, attack zinc appreciably, and zinced pipes are unsuited for their conveyance, the more so as any exposed iron forms a couple with the zinc and increases its rate of corrosion. Zinc salts being somewhat toxic, their presence in drinking water is objectionable. It has been found that zinc is sometimes attacked when in contact with cement, mortar, or brick. In the case of the first two, corrosion appears to be due to the alkaline substances present, zinc being soluble in alkalies; the latter acts by the presence in it of soluble salts, notably chlorides.

Lead oxidises with great ease when exposed to air, but the oxidation is exceedingly superficial, and the film is protective. The case is quite otherwise when carbonic acid is abundant and an organic acid present, a crust of basic lead carbonate being formed by an action similar to that taking place in the manufacture of white lead by the Dutch process (*q.v.*, Vol. II.). Complete conversion of the original lead into crude white lead may thus occur. On account of the cumulative toxic effect of lead, its presence in drinking water is very objectionable. Soft waters, especially if containing traces of organic acid—*e.g.*, moorland peat waters—dissolve the lead oxide first formed, and leave the metal exposed for further attack. Slightly alkaline calcareous waters have no corrosive effect. The solvent effect is increased or decreased by pressure (such as obtains in water mains), according to the character of the water; direct experiment is therefore necessary to decide the behaviour of any given sample. It will be seen that it is hardly possible to lay down rules for the guidance of the water engineer, who is thus ultimately dependent, as in most similar cases, on the aid of the chemist.

The character of the corrosion of aluminium is dealt with under the description of the metal itself (see *Metallurgy*). It may be said here that aluminium has been found, when pure, to resist the corrosion of most articles of food and drink. The feebleness of the toxic action of aluminium salts makes the small quantity of the metal taken into solution of no practical importance.

Nickel is more difficultly oxidisable than any of the foregoing metals. It tarnishes in moist air, but the attack is purely superficial. It resists the joint action of salt water and air better than do most common metals. Weak acids attack it with moderate ease, but it is used for cooking vessels to some extent. Its alloy with iron (75 per cent. Fe, 25 per cent. Ni), though more readily corroded than nickel, is still very resistant, and may replace brass, copper, and plated goods for many minor purposes, the more so as it can be stamped and spun.

METHODS FOR THE PRESERVATION OF STRUCTURAL MATERIALS.—The preservation of stone and brick may be effected by making them non-porous, and for this, various means may be used. Glazing is occasionally practised for bricks and tiles used for indoor work ; the objections to it for outdoor work have been stated under tiles (p. 26). By the application of a fatty or oily varnish which will soak into the stone (or brick) the surface may be rendered non-porous, but since most materials of this nature are far less durable than the stone itself, repetition of the process at intervals of a few years is necessary. Varnishes of this kind include drying oils, paraffin wax applied hot or in solution in coal-tar naphtha, and soft soap followed by an aluminium salt in order to precipitate the aluminium salts of the fatty acids of the soap in the pores of the stone. These materials, however, deteriorate the appearance of the stone. A preservative of a different order is silicate of soda applied to calcareous stones (calcium silicate and sodium carbonate being produced). The successive treatment of sandstones with silicate of soda and calcium or barium chloride is also practised (calcium or barium silicate and sodium chloride being formed) ; in this case the stone is treated with silicate of soda, allowed to dry, and then saturated with the alkaline earth chloride. A similar preservative material is obtained by the successive use of hydrofluosilicic acid and baryta, insoluble barium fluosilicate being deposited. The last-mentioned process has the advantage that no soluble salt is formed in the stone, and thus efflorescence is avoided. The only process of protecting stone which is largely used is the application of ordinary paint. With regard to the use of any preservative coating which renders the stone or brick impervious, it may be said that ordinary structures of porous untreated material, though absorbing moisture readily, allow its egress to take place equally readily, and offer no hindrance to transfusion of air through their walls. A building with impervious walls, although excluding damp from without, includes internal damp, and allows no ventilation other than through definite openings (windows, &c.) to take place.

Iron is the chief metal for the protection of which special preservative coatings are in use. Zincing for effecting this purpose has already been described. As it cannot be renewed *in situ* it is not used for permanent non-portable structures. A method of protecting, and at the same time ornamenting, iron, largely used for sign-boards and cooking vessels, consists in **enamelling** it. The details of the process are for the most part kept as a trade secret, but its principle is very simple. A preliminary glaze is given to the iron by fusing an appropriate frit (see *Pottery*, Vol. II.) on it in a muffle, and the metal is then coated with a second layer of more fusible glaze, generally coloured, by a further similar treatment. The object of the first glaze is to

provide a film intermediate in respect of its coefficient of expansion between the iron and the exterior glaze. In order to produce a sufficiently fusible glaze, lead oxide is an almost invariable constituent of both glazes. This is objectionable in the case of glazed cooking vessels, and various lead-free enamels have been proposed.

Another method, in which the protective coating is made from the iron itself, is that known as the **Bower-Barff process.** In this the goods are heated in a muffle to about 1000° F. = 538° C., and steam, superheated to about the same temperature, is admitted into the muffle. The iron decomposes the steam, becoming coated with black ferroso-ferric oxide. The depth of this coating is regulated by the length of the process, and may be as much as $\frac{1}{10}$ in. The protection is good as long as the coating is intact; it is stated that when the ferroso-ferric oxide is chipped off, the rusting of the iron exposed is more rapid than that of untreated iron. A method adapted for imparting a similar coating to articles of moderate size consists in immersion of the polished goods in a bath of melted nitre containing a little manganese oxide, and maintained at a temperature of 650° F. = 343° C. After cooling, the adhering nitre is dissolved off and the article plunged into a sperm oil bath. In another process for superficially oxidising iron to form a protective coating, the article is immersed in water and made the anode of an electric circuit, a film of ferroso-ferric oxide being formed.

None of the foregoing processes is adapted for the protection of structural materials when in place. For the preservation of structures already erected **paint** alone is available. The paint most generally in use for iron structures (bridges) is a **red oxide paint** consisting essentially of Fe_2O_3 (see *Paints*, Vol. II.). The quality of the ferric oxide used for making this paint is of much moment, some being perfectly unsuitable from the presence in it of basic ferric sulphate, which tends to corrode the iron to which the paint is applied. **Red lead paint** appears to be the best for iron work. It should be free from metallic lead (often present), which is liable to cause galvanic corrosion. The surface of the metal should be scraped scrupulously clean and free from scale, and a coat of boiled linseed oil applied before the painting proper is performed. A method of protecting iron water pipes, which is effective when carefully carried out, consists in the application of **Angus Smith's composition.** The pipes are cleaned from scale, heated to 700° F. = 371° C., and dipped into a mixture of coal tar, pitch, and a little linseed oil (about 5 per cent.), and sometimes rosin, which is heated to about 300° F. = 149° C. The pipes are dipped vertically, allowed to remain for some minutes in the bath, and then permitted to cool and drain in a vertical position. Glass-lined iron pipes are also made for conveying corrosive liquids and gases.

They are prepared by cementing glass tubes into iron pipes of slightly larger diameter, bends and T pieces being blown on to the main pipe precisely as in ordinary chemical glass blowing.

Anti-fouling compositions are largely used for protecting the bottoms of steel ships from the growth of marine animals and plants upon them. The problem of preventing the growth of marine life on the hull of a ship has been attacked from two points of view—(1) compositions have been applied which have for their object the prevention of the adhesion of barnacles and seaweed by affording an unstable foothold for these organisms. Thus a paint made of zinc oxide (white zinc) and tallow fulfils this condition. It is applied as a second coat after a preliminary coat of paint—*e.g.*, red or white lead. This material causes the growths to slip off when they have attained a certain age. For vessels of high speed such a paint is useless, as it is rapidly washed off; the second method has therefore to be employed. (2) Compositions containing a substance inimical to marine life are also in use. An example is furnished by a preparation containing mercuric oxide suspended in a shellac varnish containing crude turpentine or Stockholm tar. The varnish is soft enough to be slowly eroded, and thus to expose the mercuric oxide, which serves to poison any organism finding a temporary foothold. The use of a mixture of finely-divided zinc and mercuric oxide, made into a soft varnish, has also been suggested. It is claimed that this composition is effective by reason of the fact that when the mercuric oxide dissolves, mercury is deposited on the zinc, and when the zinc dissolves mercury is left in the varnish, and dissolves more slowly than mercuric oxide. A method for protecting iron, more particularly used for boilers (*v.i.*), consists in attaching to the metal, plates of a substance electropositive thereto—*e.g.*, zinc, the process being equivalent to local galvanising. It is obvious that this process is only effective when the whole of the surface to be protected is immersed as in the case of a boiler; the attack is then confined to the electropositive metal—*e.g.*, the zinc. The same system has been applied to the protection of copper dye baths, the corrosion of which is objectionable on account of the effect of the traces of copper upon the colour of the contents of the vat.

Ornamental iron goods are often plated electrolytically with nickel. As nickel is electronegative to iron the coating is only effective as long as it is intact; when injured it enhances corrosion instead of preventing it. The same is true of plating with copper on iron.

No other metal is at once so freely exposed and so corrodible as iron, and special methods of protection are therefore rarely used for copper and its alloys, or for lead, zinc, &c. When plating with copper, nickel, silver, or gold is adopted, it is rather for ornament than for protection.

The **preservation of timber** depends largely on the protection of the wood from moisture which favours the growth of the low organisms concerned in its destruction. To this end the wood should be well ventilated, and, it is said, kept from contact with mortar. Timber must not be used before the sap is dried out of it since this contains easily fermentable substances. The sap can be replaced by a preservative—*e.g.*, coal-tar creosote, wood creosote, zinc chloride, mercuric chloride, or copper sulphate. Such treatment becomes necessary when the wood is to be used in wet situations or under water. The most direct method for the preservation of wood consists in applying a pump to the butt end of the freshly-felled tree and injecting zinc chloride solution of specific gravity 1·01, the sap being driven to the smaller end of the tree and gradually extruded. (The same process may be adapted so as to colour timber; by the injection of weak sulphuric acid a tree may be coloured brown, or mahogany red by nitric acid.) A larger proportion of zinc chloride remains in the butt end than in the distal end, and thus the preservative effect is somewhat irregular; the chief merit of the process consists in the ease with which timber can be treated at the spot where it has grown, without transport being requisite. Zinc chloride is also used in the same manner as creosote, the application of which is described below; the solution of zinc chloride thus employed is known commercially as **Burnett's fluid.** Mercuric chloride may be substituted for zinc chloride, its application being known as **kyanising.** Copper sulphate, forced into the wood by leading a solution of the salt from an elevated reservoir by means of a pipe which is inserted into the log, is also used, the method being known as **Boucherie's process. Creosoting** is most largely used for preserving timber, especially railway sleepers. Coal-tar creosote (see *Coal-tar*, Vol. II.) is generally used in this country, the grade required being a dark mobile oily liquid of specific gravity 1·035 to 1·055 and containing about 10 to 15 per cent. of tar acids (phenol and its homologues), to the presence of which its preservative action is partly due. Its efficiency largely arises, however, from the fact that it serves to fill the pores of the wood with an insoluble inert oil which prevents the entrance of water and the growth of organisms. Creosoting is conducted by introducing the well-seasoned timber into steel cylinders about 36 feet long and 6 to 7 feet in diameter. The air is then exhausted from the cylinder until a pressure of about 2 lbs. per square inch remains. The creosote oil is heated to 50° C. = 122° F., run into the cylinder, and forced into the wood by a pressure of 120 to 150 lbs. per square inch. The pressure is maintained for several hours, the timber, if pine, absorbing about 12 lbs. of oil per cubic foot of wood. Large pieces of wood often show a core free from oil, as uniform impregnation is difficult. In America, where but little coal is

carbonised and wood is cheap, wood creosote has been successfully used for the preservation of piles exposed to the attack of the teredo. The character of the oil used may be gathered from the products said to be yielded on distillation, as shown by the following analysis :—

	Per cent.
Water,	2·79
Neutral oil,	13·16
Crude creosote (wood-tar acids),	17·00
Heavy oil,	26·55
Paraffin wax,	25·97
Coke,	5·78
Uncondensed,	8·75
	100·00

The foregoing methods are analogous in principle to the impregnation of stone with preservative solutions (p. 43). Other methods of preserving wood consist in applying a superficial protective coating. It is important that this should not be done until the wood is well seasoned, since if moisture be prevented from escaping the wood will rot. ("Dry rot" is believed to be due to the action of an organism.) Coatings of this kind include paints and tar (coal or wood, the latter being more effective). Another method adopted for wood—which is comparable in principle with the Bower-Barff process, inasmuch as the material to be preserved itself furnishes the preservative coating—consists in superficial charring. This is chiefly used for preserving posts and stakes to be inserted in moist soil.

CHAPTER II.

THE CHEMISTRY OF THE SOURCES OF ENERGY.

EVERY form of energy on this planet can be traced to one of three sources. These are (1) the heat of the sun, (2) the rotation of the earth, (3) the internal heat of the earth.

The first is at present by far the most important. The kinetic energy pouring from the sun as heat and light can be with difficulty industrially utilised. The energy which has been derived from the sun and become potential in the form of fuel is readily utilised, and has been hitherto the only practicable source of energy for industrial purposes. The second is of minor importance, being represented only by the energy manifested by the rise and fall of the tide; no successful attempt has hitherto been made for its utilisation. That the third undoubtedly exists as a source of energy is proved by the occurrence of volcanic phenomena; its utilisation belongs to the future.

Potential energy in the form of stored heat from the sun will, therefore, be chiefly considered in the ensuing pages; the other and minor sources of energy will be dealt with subsequently.

Fuel may be defined as any substance capable of exothermic oxidation with sufficient rapidity to leave an available balance of energy after the leakages of energy surrounding the point of combustion (*e.g.*, radiation, convection, and conduction) have been supplied. It is obvious that *cæteris paribus* the available balance will be larger the more concentrated the fuel—*i.e.*, the smaller the quantity of matter it contains which, on the one hand, is incapable of contributing to its exothermic oxidation, and, on the other, augments the loss by leakage. From this it follows that for two equal weights of the same oxidisable material, the fuel which contains, in addition to the oxidisable material, the smaller quantity of inert matter will tend to give a higher thermal efficiency; for the larger weight and bulk of the more impure fuel will lead to larger leakage by conduction, convection, and radiation. By far the greater part of the fuels industrially used consists of carbon; elements whose combustion is also used in minor degree are hydrogen (chiefly in union with carbon, but also in the free state), sulphur, as native sulphur (Vol. II.), and as pyrites (*cf.* concentration of vitriol in the Glover tower, Vol. II.), and silicon, phosphorus, and manganese in the Bessemer converter (see *Ingot Iron* under *Metallurgy*). The following are the chief kinds of fuel :—

Class of Coal.	C.	H.	O.	Coke.	Character of Coke.	Sp. gr. of Coal.	Calorific Value.*
	Per cent.	Per cent.	Per cent.	Per cent.			Calories.
Dry coals burning with a long flame,	75 80	5·5–4·5	19·5-15	50-60	Pulverulent or slightly sintered,	1·25	8,000-8,500
Caking coals with long flame (gas coals),	80 85	5·8–5	14·2–10	60-68	Intumesced ; semi-fused,	1·28–1·30	8,500-8,800
Caking coals proper, forge coal, coking coal,	84-89	5·5-5	11-5·5	68-74	Coherent and fairly dense,	1·30	8,800-9,300
Caking coals with short flame,	88-91	5·5–4·5	6·5–5·5	74–82	Coherent and very dense,	1·30-1·35	9,300-9,600
Anthracitic or lean coals burning with short flame,	90-93	4·5–4	5·5-3	82–90	Pulverulent or slightly sintered,	1·33-1·40	9,000-9,500

* By this is meant the number of kilos. of water which the combustion of 1 kilo. of coal will raise from 0° to 1° C.

A. **SOLID FUEL.—COAL.**—Many varieties of carbonaceous matter, known generically as coal, are used as fuel. Of these **coals**, considered as distinct from **brown coals** and **lignites**, the foregoing groups may be distinguished, according to Grüner's classification which is based upon the technical use of the coals.

The different qualities which are found have no clear line of demarcation between them, so that their classification, as will be seen from the table, is necessarily somewhat arbitrary.

The figures tabulated above are for ideal coals, free from sulphur, ash, water, and nitrogen, which are constituents of all actual coals, and range from 1 to 30 per cent. for ash, 0·5 to 2 per cent. for sulphur, 0·1 to 9 per cent. for water, and 0·2 to 2 per cent. for nitrogen. A good coal will not contain much more than 5 per cent. of ash, 1 per cent. of sulphur, 2 per cent. of water, and 1 per cent. of nitrogen. Besides the above ordinary varieties of coal, two kinds need special mention. True **anthracite** is distinguished from anthracitic coals by containing a still higher percentage of carbon and a still smaller percentage of oxygen and hydrogen. In appearance it is deep black, but it does not stain the fingers in the manner characteristic of bituminous coal. Its fracture is conchoidal, and its specific gravity may be as high as 1·7. It burns with a very short flame, and shows no tendency to sinter in the fire, but often decrepitates in the act of burning. Seeing that the amount of flame with which a given coal burns increases with the content of hydrogen, and that the larger the flame produced the more easily a coal is kindled, it follows that anthracite is nearly flameless and is also difficult to ignite, a circumstance militating against its domestic use. The second kind of coal needing special description is **cannel**, which is distinguished by a large content of hydrogen over and above that corresponding with the oxygen in the ratio H_2:O (*v.i.*), and therefore available for gas production (see *Destructive distillation*, Vol. II.). Analyses of these two extremes of the whole series of coals are as follows:—

	C.	H.	O.	N.	S.	Ash.	Water.
	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
Swansea anthracite,	90·58	3·60	3·81	0·29	...	1·72	...
Boghead cannel, .	65·3	9·1	5·4	0·7	0·1	18·6	0·5

The total amount of heat that can be produced by the combustion of a given weight of coal can be ascertained either by calculation from the composition of the coal or by direct experiment. On account of incomplete knowledge of the conditions in which the constituents of coal exist, the calculated **calorific value** is only approximate to the truth, being generally considerably below the experimental value. It is customary to determine the percentage of C, H, N, S, and O in the coal by analysis, and to

calculate the calorific value on the basis of the facts that the complete combustion of 1 kilo. of carbon evolves 8,080 Cal., while 1 kilo. of hydrogen gives 34,400 Cal., and that the heat evolved by the combustion of the sulphur is so small as to be usually negligible. Further, it is assumed that the oxygen is present combined with hydrogen in the same proportion as it is in water, and that the amount of hydrogen thus combined is not available for the production of heat when the coal is burned. Thus the number of calories evolved by the combustion of 1 kilo. of coal will be given by the formula $8{,}080\ C + 34{,}400\left(H - \frac{O}{8}\right)$, where C, H, and O represent the respective parts by weight of these elements in one kilo. of coal.

The direct determination of the calorific value of the fuel may be made by burning a known weight with a mixture of oxygen-yielding substances, or in a stream of oxygen, or in compressed oxygen in a confined space, the whole apparatus being in all cases immersed in a known weight of water, the rise of temperature of which is a measure of the calorific value of the fuel. For practical reasons the last plan is the best. It can be carried out in the apparatus shown in the figure (Fig. 4). This consists of a steel shell, A, lined with white enamel, and having a capacity of 650 c.c.; a cover provided with a lead washer, screws on to the body of the shell. A weighed quantity of fuel—*e.g.*, 1 gramme—is placed in a capsule, B, and oxygen is admitted from a cylinder of the compressed gas through the tube, R, made of nickel-iron (pp. 24 and 42), and serving as a screw-valve, until the pressure, as shown by a gauge, is 20 to 25 atmospheres. The valve is then closed, the shell immersed in the calorimeter, and the fuel ignited by means of an electric current traversing a fine iron wire spiral which passes through the fuel and is attached to the two platinum rods, D, which support the capsule. The current is conveyed through the insulated conductor, E, which passes through the lid, the other electrode being attached to the shell. The rise of the temperature of the water in the calorimeter during the experiment is noted by means of a delicate thermometer.

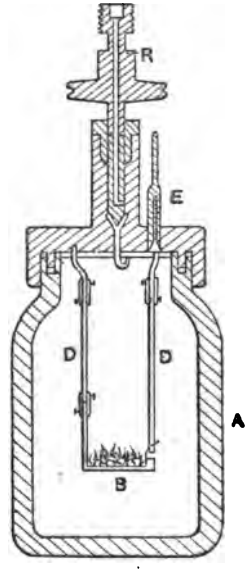


Fig. 4.
Calorimetric shell.
A, Steel shell; B, capsule for containing the fuel; R, tube for admission of oxygen; D, E, electric leads.

The utility of a coal depends not only on its calorific value, but on its character in respect of its content of bituminous gas-yielding matter, and of the nature of the coke formed by its partial combustion or destructive distillation. The progress of combustion of a coal in an ordinary furnace involves the destructive distillation of a portion of it, whereby gases are evolved which determine the nature of the flame produced. Judgment of the properties of a given coal in this respect is based on the figures yielded by its proximate analysis, which is effected by heating a weighed quantity of the coal in a covered crucible, and estimating the fixed carbonaceous matter, plus the ash, as coke. (The yield of coke by different kinds of coal has been given in the tabular classification of coals—p. 49.) The ash is also determined, and the difference between this and the coke constitutes the fixed carbonaceous matter.

It may be broadly stated that coal is used for steam-raising, household fires, gas-making, and metallurgical operations. For the first of these uses a hard "steam coal" of a semi-anthracitic kind is most esteemed, as it has a high calorific value, produces little ash and clinker, and does not smoke. For household fires a more freely burning and more bituminous coal is requisite; one which cakes is economical, as the fire can be readily damped down. For gas-making, bituminous coals with a fair content of hydrogen are requisite (see *Destructive distillation*, Vol. II.); the quality of the coke formed is of minor importance. For metallurgical use much coal is coked (see *Destructive distillation*), and for this purpose caking bituminous coal is generally preferred. Both flaming and anthracitic coals are used, according to the nature of the work to be done. With regard to the common impurities of coal, it may be said that ash should be present to a minimum extent, as the grate is blocked and impeded by the dust and clinker produced by a fuel rich in ash, which, moreover, causes a small waste of heat in being raised to a high temperature during combustion and being removed from the grate before it has given up this heat. Sulphur is also objectionable on account of the contamination of the surrounding air by chimney gases containing the sulphur of the coal in the form of sulphurous and sulphuric acids. Water is also objectionable, as it has to be evaporated, involving the useless expenditure of heat. Nitrogen is not of much detriment in coal, as the waste of heat occasioned by raising its temperature is not serious (as it is always present in only small proportion). In gas coals it has a certain commercial value, in that a portion of it is recovered as ammonia (see *Destructive distillation*). Attempts have been made to recover the nitrogen in a useful form from the coal burned in ordinary furnaces, but success has only been achieved hitherto in the case of blast furnaces. Coal suffers diminution of its calorific value by exposure to air and moisture (*weathering*). This alteration is due

to oxidation, and is accompanied by a gain of weight, which in extreme cases may amount to as much as 4 per cent. Pyrites, which is constantly naturally present in coal, also suffers oxidation to some extent, but is not as fruitful a cause of spontaneous ignition as has been supposed, this phenomenon being due to the oxidation of the less stable carbonaceous constituents of the coal. Such spontaneous ignition takes place more readily when the coal is crushed and exposed to a warm atmosphere, as in the bunkers of a steamship. The quality of coal may be improved by systematic washing; the coal is thus graduated in size, and, by taking advantage of the difference of specific gravity between coal on the one hand and shale and pyrites on the other, a diminution of ash content is also effected, the sulphur (due to the pyrites) being correspondingly reduced in amount. The general mechanical arrangements of apparatus for **coal-washing** are identical in principle with those used for sizing and concentrating ores (see *Gold*).

COKE is carbonised coal containing the whole of the ash of the original coal and the greater part of the carbon, but comparatively small amounts of H, O, S, and N. Two classes of coke may be broadly distinguished. The first is that which is manufactured by processes of which the coke is the main product, and the other substances formed by the destructive distillation of the coal are the bye-products. It is made in coke ovens for metallurgical consumption; its manufacture is treated of in the section dealing with destructive distillation (*q.v.*, Vol. II.). The second class of coke is that obtained as a bye-product in carbonising coal for gas-making, where the main products are gas and tar. "Oven coke" is denser and of greater mechanical strength than "gas coke," and is therefore better fitted to carry the burden of the blast furnace (see *Iron*). Moreover, oven coke resists the oxidising action of hot CO_2 better than does a coke of looser structure, and thus suffers less waste in the upper part of the blast furnace. These qualities warrant the metallurgical use of oven coke in spite of its greater cost; the cost has been largely diminished of late years by the collection of bye-products (see *Destructive distillation*, Vol. II.). Good dry oven coke contains about 90 per cent. C, 1 to 2 per cent. H, 1 to 2 per cent. O, 1 per cent. S, 1 per cent. N, and 5 per cent. of ash; it has a calorific value of about 8,000 Cal.; it generally contains 2 to 3 per cent. of moisture, but this amount is exceeded when it has been carelessly quenched after coking. Seeing that the yield of coke is about 66 per cent. of the weight of the coal carbonised, the percentage of ash will be increased in inverse ratio. Thus a coal containing 5 per cent. of ash will yield a coke with 7·5 per cent. For blast furnace use, the amount of ash should not exceed 5 per cent., and for metallurgical use generally the percentage of sulphur should be as low as possible —1 per cent. or under. Not only is ash in coke objectionable as

being valueless, but it is actively injurious in some instances on account of its chemical nature. The ash of most coals, and therefore that of the corresponding cokes, consists largely of silica, alumina, and ferric oxide—all substances capable of acting as acid oxides when brought into contact with powerful bases (*e.g.*, lime) at high temperatures; consequently, wherever the manufacture of a substance such as quicklime or hydraulic cement involves the admixture of the fuel with the raw material to be burned, there is ample opportunity for the ash of the former to combine with the latter, to its detriment (see *Lime* and *Cement*, Vol. II.). As much gas coke contains a large amount (up to 30 per cent.) of ash, its chief manufacturing use—in cement-making—is attended by considerable drawbacks; its cheapness is its main recommendation. Among the smaller uses to which coke is put are the heating of metals and tools, and of articles to be brazed, where the comparatively dirty flame of coal would be unsuitable. As coke still contains some sulphur, however, gas, wood or charcoal is preferable for the foregoing purposes. Thus, in tempering machine guns, wood is used as fuel on account of its freedom from sulphur. The specific gravity of coke is from 1·2 to 1·9, rising with increased percentage of ash, but the texture of the fuel is so porous that this datum is but little guide to the space which the coke occupies in the furnace. In any case, ample room must be provided for its adequate combustion. Apart from the determination of ash and sulphur, the valuation of coke can be made by testing it by the calorimeter in the manner described for coal, and then its suitability must be judged by its texture and mechanical strength, according to the use to which it is to be put. Coke, on account of its comparative freedom from sulphur, its smokelessness, and the fact that in burning it neither fuses nor cakes, is used in place of coal for purposes in which any or all of these properties are desirable, in spite of its greater cost per heat unit.

BROWN COALS AND PEAT.—According to the age of the geological formation in which coal occurs, the character of the products of distillation of the coal varies. The older coals have been so far altered that the original grouping of the elements in the parent vegetable matter, which gives rise to acid products of distillation (see *Destructive distillation*—wood and peat, Vol. II.), has been modified, with the result that the products of distillation are alkaline from the presence of ammonia and other nitrogenous bases. Coals belonging to a later period have been less altered from the original composition of the woody matter from which they have been derived, and, like wood, yield a distillate containing acetic acid. Three classes of these later coals (*brown coals*) may be distinguished:—(1) **Brown coal**, with lustrous conchoidal fracture, is the oldest and most nearly related to ordinary bituminous coal. Handsome specimens of this sub-

stance are used for ornament as *jet*. A typical composition of the coal, free from ash, is about 75 per cent. C, 5 per cent. H, and 20 per cent. O, small quantities of nitrogen and sulphur being, as usual, present. (2) **Earthy brown coal,** of earthy fracture, as its name implies, containing in the ash-free coal 71·72 per cent. C, 5·76 per cent. H, and 22·50 per cent. O; it is usually rich in ash and water. (3) **Ligneous brown coal** (*lignite* *), of fibrous fracture, showing a definite woody structure and containing (in the ash-free material) 60 per cent. C, 5 per cent. H, and 35 per cent. O. Brown coal, which is mined on a large scale in Austria and Germany, has a very variable calorific value on account of its fluctuating content of water and ash; 4,000 to 6,000 Cal. may be taken as ordinary limits. It burns with a

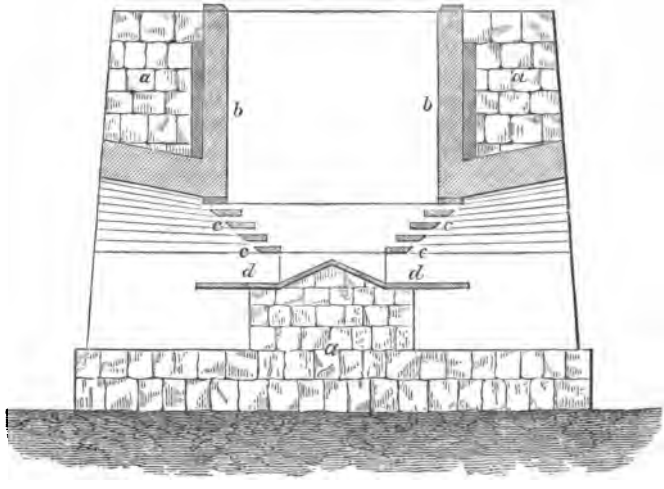


Fig. 5.—Kiln with step grates.

considerable amount of flame, and is best used (especially the earthy variety) on *step-grates*—that is, grates with firebars arranged in a terraced form, as shown in the figure, which illustrates the system adapted to a kiln. *a* represents the masonry of the kiln. The steps of the grate are shown at *c c*. The ash falls on to the bottom of the furnace, *d*, whence it is removed, and the fuel is continuously fed so as to slide down the sloping set of firebars between which the air for its combustion enters.

The most recent formation of a coal-like fuel is that exemplified by the peat bogs of Ireland and other countries. The change from fresh vegetable matter is not far advanced; the original

* Some writers in this country misuse the word "lignite" to include all brown coals.

material in this case is for the most part moss. The composition of **peat** (free from water and ash) is about 60 per cent. C, 6 per cent. H, 34 per cent. O, and from 1 to 2 per cent. N. The ash varies from 5 to 50 per cent. of the dried material. Air-dried peat contains from 15 to 20 per cent. of water, and the freshly cut material contains about 90 per cent. of its weight of water. When air-dried its calorific value is from 3,000 to 5,000 Cal. On account of its bulk it has to be compressed before it can be used as a fuel, and the cost of preparation forbids its use except on the spot where it is cut. It has, however, found a limited application, in peat districts, for feeding producers (*q.v.*).

Briquettes.—Small dusty fuel, obtained as a bye-product in winning and sifting coal, can only be burnt in special forms of furnace—*e.g.*, those provided with continuous mechanical stoking apparatus, or with step grates (*v.s.*)—unless previously moulded into blocks or briquettes which constitute so-called **patent fuel.** The fine stuff is washed and sifted, mixed with about 6 per cent. of pitch, tar, glutin or treacle, and moulded into bricks under a pressure of 5 to 10 tons per square inch. Brown coal has usually to be dried before it can be moulded, and can then be shaped without the addition of cementing matter, as the resinous substances which it contains are sufficiently cohesive at the temperature employed (75° C. = 167° F.).

Briquettes made with pitch soften at comparatively moderate temperatures, while those cemented with soluble binding materials are disintegrated by wet. An ideal binding material has still to be found.

WOOD AND CHARCOAL.—In this country wood is too scarce to find application as fuel, but it is largely burnt in lands still containing much forest. Wood free from water contains 50 per cent. C, 6 per cent. H, 42 per cent. O, 0·1 per cent. N, and 1 per cent. ash. Air-dried wood contains 15 to 20 per cent. of water; the content of water in freshly cut wood is from 20 to 50 per cent. Wood is not capable of giving a very high temperature when burnt, but it kindles more easily than coal, and burns with more flame. It has a calorific value (in the air-dried state) of about 3,000 Cal. Just as coal may be advantageously converted into coke, producing a non-flaming fuel, so can wood be carbonised to produce charcoal (see *Destructive distillation*, Vol. II.). The progressive change of wood to charcoal as the temperature of carbonisation increases is shown by the table on the next page for the production of charcoal from black alder.

Brown charcoal, as might be expected, is more easily kindled than black charcoal. It is only used for the preparation of certain classes of gunpowder. *Black charcoal* increases in difficulty of ignition as the temperature at which it has been carbonised rises. Good black charcoal has a calorific value of about 8,000 Cal. Its utility depends on its smokelessness and

its freedom from smell and sulphur, on account of which properties it is used (on the Continent) for domestic heating, and in this country for fine metal work and similar minor purposes.

Temperature.	C.	H.	O.	Ash.	Character of Product.
	Per cent.	Per cent.	Per cent.	Per cent.	
150° C. = 302° F.	47·51	6·12	46·29	0·18	Imperfectly carbonised.
200° C. = 392° F.	51·82	3·99	43·96	0·23	
270° C. = 518° F.	70·45	4·64	24·19	0·85	Brown charcoal.
350° C. = 662° F.	76·64	4·14	18·44	0·61	Black charcoal.
440° C. = 824° F.	81·64	1·96	15·24	1·16	
945° C. = 1,733° F.	81·97	2·30	14·15	1·60	
1,045° C. = 1,913° F.	88·14	1·41	9·26	1·20	
1,775° C. = 3,227° F.	96·52	0·62	0·94	1·94	

B. **LIQUID FUEL.**—Liquid fuel is of minor importance in this country, as its price prevents its successful competition with coal for any but special purposes. It may be stated generally that liquid fuel has the advantage of being less bulky than coal for a given calorific value, of being free from ash, and of being more completely under control while burning, thus facilitating regulation of the fire, and, when used under a boiler, of the steam pressure. No stoking in the ordinary sense is requisite with liquid fuel, and, therefore, opening of fire doors and admission of cold air are avoided. The only successful methods of burning liquid fuel comprise the two plans—(1) feeding by natural flow down an inclined gutter; this is adapted for viscous liquids, such as tar; (2) injecting by an air or steam jet in the form of a spray. A "spray maker" of good design is that used in the Priestman oil engine, and shown in Fig. 6. The oil is injected through a central tube, and the air impinges upon the jet of oil in an annular stream, the oil being thus broken up and ejected in the direction of the arrows as a fine spray. The charge of air and oil is also heated in a vapourising chamber by means of the exhaust gases of the engine. In this country, tar and creosote oil (dead oil; see *Coal Tar*, Vol. II.) are used, while in Russia the petroleum still-residue, *astatki* (see *Petroleum*, Vol. II.) is employed. The ultimate composition of the materials used as liquid fuels is similar for all kinds. Thus, taking the combustible constituents, tar contains about 85 per cent. C and 5 per cent. H; creosote oil 83 per cent. C and 10 per cent. H; astatki 85 per cent. C and

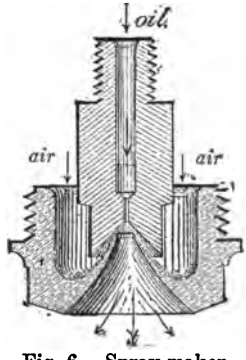


Fig. 6.—Spray maker.

10 per cent. H. Astatki has a calorific value of about 11,000 Cal., as compared with 8,000 to 9,000 for good steam coal; the other liquid fuels give slightly lower values. It will be seen that astatki is the best liquid fuel, but it cannot be remuneratively imported into this country. Once-run Russian petroleum (*q.v.*) is imported for gas-making, but can barely compete with creosote oil. Crude petroleum is not imported for use as liquid fuel, both on account of the danger of transporting and handling a material containing constituents of low flashing point, and also because it is more profitably distilled fractionally to obtain lighting and lubricating products. Of definite products of fractionation, none but the ultimate residue is cheap enough for use as fuel. In the injection process for burning liquid fuel, mentioned above, the function of the jet of steam, when this is used, is purely to "atomise" the oil, for it obviously cannot be supposed, as has been ignorantly stated, that the steam contributes to the heating effect of the fuel. Any heat from the combustion of hydrogen with oxygen which may be obtained by the dissociation of the steam, is exactly counterbalanced by the absorption of heat previously needed to effect the dissociation.

Where compactness in storage is important—*e.g.*, on board ships of war—the small bulk of liquid fuel presents a notable advantage. One ton of liquid fuel occupies about three-quarters the volume occupied by a ton of coal, and as its heating efficiency is one and a-half times that of an equal weight of coal, it follows that the liquid fuel requisite for a given horse-power takes up one-half the space required by coal for the same output. Attempts have been made to prepare liquid fuel in a form capable of use in an ordinary furnace. Two methods of "solidifying" petroleum have been devised for this purpose. The first depends on the fact that when soap is added to an unsaponifiable oil, such as petroleum, the whole mass becomes gelatinous, not from any chemical action on the petroleum, but simply from the property of soap of forming an apparently homogeneous jelly with many liquids, water being a case in point. The jellies of the greatest consistency are made by forming the soap *in situ* by adding a saponifiable oil or a fatty acid to the petroleum and then the requisite amount of alkali. The jellies made by the aid of castor oil and coco-nut oil are particularly firm and coherent. The second plan for solidifying petroleum consists in absorbing the liquid by a porous material in the manner in which nitroglycerin is solidified by absorption in kieselguhr (see *Explosives*, Vol. II.). Since siliceous matter of this kind would remain on combustion as ash, some combustible material, such as cheap vegetable fibre—*e.g.*, peat—is to be preferred. Solidification by means of a material of this nature may be aided by the addition of soap. Products of both types

are liable to ooze in the furnace before igniting thoroughly, and their stability when stored in hot places is also doubtful. The fact that Russian petroleum contains naphthenes, which are capable of oxidation to acid products by air in the presence of sulphuric acid, makes it possible that should a demand arise for solidified petroleum it may be prepared by saponifying such acid substances *in situ*. (The production of soap from acid oxidised products of petroleum has, however, not yet been accomplished on a commercial scale.) The adoption of "solidified" liquid fuel on a considerable scale is improbable, as by the solidification the advantages obtained by the use of liquid fuel are sacrificed, and a direct comparison with coal becomes even more favourable to the latter.

Of greater importance, so far as this country is concerned, than its use under the boilers of steam engines, is the application of petroleum to the direct provision of energy for conversion into mechanical power by explosive combustion in the cylinder of an oil engine. For this purpose the oil may either be a low boiling fraction of petroleum—*e.g.*, "gasolene" (*q.v.*)—such as is capable of volatilisation even at ordinary temperatures, so that its vapour can be mixed with air, and introduced in this manner into the explosion cylinder, or an oil of higher boiling point—*e.g.*, "kerosene" (*q.v.*)—in which case it must be first "atomised," and the sprayed liquid mixed with the air with which it is to be exploded.

The portability of petroleum, as compared with compressed gas even of the richest kind (oil gas), and the practicability of directly utilising its energy for the production of mechanical power, are valuable properties which are taken advantage of in the case of launch engines, and in isolated places where power is wanted without the risk attendant on trusting a boiler to unskilled hands, and where gas is not available. With regard to the chemical aspect of this utilisation of liquid fuel, it may be said that gasolene should be a fairly homogeneous fraction of petroleum—*i.e.*, it should distil within narrow limits in order that the rate of volatilisation may be uniform, and that no residue of heavy difficultly volatile oil may be left in the vessel in which the air is "carburetted" before explosion. Similarly, kerosene should be free from acid (due to careless refining), and from heavy fractions tending to condense and carbonise at the moment of explosion. It may be added that the variable character of commercial oils renders it desirable that they should be systematically examined to ascertain whether they comply with the limits specified.

In cases where gas is not available, and solid fuel is inconvenient, petroleum (both gasolene and kerosene) is used directly for heating either as carburetted air, or burnt from a wick; portable experimental and assay furnaces have been constructed to use liquid fuel in this manner.

C. **GASEOUS FUELS.**—With the exception of natural gas (*q.v.*) all gaseous fuel is prepared artificially, and its preparation involves the consumption of rather more energy than appears in the product in an available form, since the usual inevitable loss attending the conversion of energy must occur. Thus coal can be either burnt as solid fuel, or completely gasified and then burnt. Taking into account the energy necessary for the gasification, the gasified coal must contain less total energy than the coal when solid, and no gain of energy can possibly take place. Nevertheless, it often happens that the advantages of gaseous fuel outweigh commercially the loss of energy involved in its formation. The main advantages of gaseous fuel of all kinds will be evident from the following considerations :—

1. Gases can be readily, rapidly, and perfectly mixed, and thus the quantity of air exactly adjusted to that of the gas to be burnt, whereas solid fuel, burning exclusively at its surface, needs excess of air in order that its combustion may be complete, and the formation and final escape of imperfectly oxidised products—*e.g.*, CO—avoided. Were it possible to allow the air to remain in contact with the burning solid fuel until the reaction between them became complete, no excess of air beyond the calculated amount would be requisite, but under practical conditions the necessary sojourn would be unduly lengthy, and incompatible with the conditions necessary for continuous combustion. In gaseous firing, therefore, the restriction of the air supply to a small excess over the calculated quantity diminishes the weight of the final flue gases, as compared with those given by solid fuel, and consequently, for a given temperature of escape, decreases the quantity of heat which they carry away.

2. Firing with gaseous fuel can be regulated with the same ease as that already mentioned as characteristic of liquid fuels, and in addition can be used with excess or defect of air as may be desired, to yield an oxidising or a reducing atmosphere.

3. Freedom from ash and soot, a matter of importance for many industries, is secured by gaseous firing.

4. Gaseous fuel adapts itself readily to the use of regenerative heating, and thus lends itself to the production of high temperatures.

5. Small fuel, containing much ash, and bulky fuel—*e.g.*, peat—are more readily dealt with by preliminary gasification than by direct burning.

Gaseous fuel can be produced from solid fuel by processes which may be divided into two classes—(*a*) destructive distillation involving the formation of a fixed carbonaceous residue, and (*b*) complete gasification with the removal of the whole of the fuel (with the exception of the fixed mineral constituents) as gases.

COAL GAS, which is the only gas made by destructive dis-

tillation, and distributed on a large scale, is not primarily prepared for heating and as a source of power, but it is nevertheless used as a domestic fuel and for supplying moderate quantities of mechanical energy by means of the gas engine as intermediary. Its production and composition are described in the section on *Destructive distillation*, Vol. II.

For the production of heat as a warming and cooking agent it is burnt in two distinct ways—(1) from jets or slits giving a luminous flame (with or without a chimney), and (2) from burners of the bunsen or "atmospheric" type, in which it is mixed with air at a point anterior to that at which it is burnt. The total calorific effect is constant, however the gas is burnt, provided its combustion be complete. Choice between the methods turns on their convenience under given conditions. For rapid heating in contact with the flame—*e.g.*, boiling—the non-luminous flame is necessary, as it does not deposit soot on the vessel heated, which would form a non-conducting layer. Soot thus deposited also obviously means the loss of fuel. Where heating by radiation is contemplated, the gas may be burnt with a luminous flame, preferably with the aid of a chimney, as in an argand burner (the total radiant heat being then about 12 per cent. of the total chemical energy of the gas). In such cases the products of combustion are only as deleterious as those of ordinary unprotected gas jets used for lighting purposes, and a flue may sometimes be dispensed with in a well-ventilated room. For burners of this type used for heating rooms, an arrangement to condense the water produced by the combustion of the gas is sometimes provided, and undue moistening of the air of the room thus avoided, but the CO_2 and other gaseous products of course escape. Heating by radiation may also be effected by the use of a non-luminous flame caused to heat a refractory material—*e.g.*, iron, platinum, asbestos, or fire clay—to incandescence. With such stoves a flue should always be used, as at the cooler parts of the material to be heated, combustion is checked by contact of the flame with a solid body, and the usual products of checked combustion—among which are acetylene and carbon monoxide, gases of markedly toxic properties—are formed. Evidence of such checked combustion is given by the sense of smell in the air of a room in which a kettle of water is being heated over a common burner of the bunsen type. Even when coal gas is burnt from the best form of heating or lighting burners which have no device to carry off their products of combustion, the air of the room is liable to serious contamination. Thus each cubic foot of ordinary coal gas yields about 1 ounce of water and 0·57 cubic foot of CO_2. As a common flat flame burner consumes about 5 cubic feet per hour, the quantity of the main products of combustion becomes considerable in a well-lighted room. The amount of SO_2 produced per 100 cubic feet of gas burnt is about 20 grains. The

effect of these products of complete combustion is enhanced by that of unoxidised or imperfectly oxidised products, hydrocarbons and CO, which invariably appear in small amount. The percentage of CO_2 in normal air is 0·03 per cent., and the approximation to normal condition of the air of a given room is generally gauged by its content of CO_2. This should not be above 0·1 per cent., but is frequently exceeded when much gas is burnt. The toxic effect of CO is much greater than that of CO_2, but the question of its presence in coal gas becomes of importance only when an escape of unburnt gas (which contains about 6 per cent. of CO) has occurred (see *Water Gas*).

The calorific value of coal gas averages 170 Cal. per cubic foot —*i.e.*, 673 British thermal units.* The chemical energy of coal gas can be directly converted into mechanical work by means of the gas engine. In this machine a mixture of gas and air (1 volume gas to 9 to 11 volumes air) is exploded behind a piston, and the longitudinal motion thus imparted to the piston converted into circular motion as in a steam engine. The use of a sudden and violent impulse, such as is implied in the word "explosion," does not on *a priori* grounds recommend itself as an economical method of obtaining power, but it must be understood that the explosion is of a more gradual kind, on account of the dilution of the charge and the rapid enlargement of the chamber in which it takes place (due to the advance of the piston) than that characteristic of a shattering explosion produced by a blasting explosive. There is a difference in degree, but not in kind, between the ignition of a gas engine charge and that of a rifle or piece of artillery, the propulsive effect in some of the larger guns partaking of the nature rather of a steady, though extremely vehement, push than of a violent shock. Another cause for the gradual character of the impulse in a gas engine, is the prevention of instantaneous and complete explosion of the mixed gases in its cylinder by the raising of their temperature, owing to an explosion of part of them, to the temperature of dissociation of their products of explosion, inhibiting further combination. As the piston moves the gases expand, doing work, and their temperature falls, allowing fresh combination of unused portions, until the dissociation temperature is again reached. The process of explosion is therefore automatically controlled, continuous and steady, and the power is exerted fairly uniformly during the stroke.

The gas engine, though more efficient than the steam engine, still leaves a good deal to be desired. The average output of mechanical work corresponds with 10 to 15 per cent. of the energy present in the coal gas. This low result is largely caused by the necessity for cooling the working cylinder (by means of a water-jacket). The necessity arises from the difficulty of finding

* This represents about one-fifth of the calorific value of the parent coal.

a lubricant which will both retain a fair degree of viscosity (see *Lubricants*) and not suffer decomposition at high temperatures. Another reason for cooling the cylinder is the decreasing strength of structural materials (metals notably) with rise of temperature. It is obvious that a large fraction of the energy of the exploded gas goes to warm water instead of performing mechanical work. Combustion in a gas engine is usually nearly complete,* but an exhaust into the open air is of course as necessary as with a gas stove. The economical consumption of coal gas in a gas engine is seldom of great importance, as for larger powers, where the cost of energy, apart from other charges, becomes a tangible item, coal gas is not used, producer gas (*q.v.*) being substituted for it.

There is another use of coal gas as a source of energy which requires comment—viz., the supplementing of the effect of compressed air, supplied from central stations as a motive power in a few cities. The air before entering the motor is heated by a gas burner, and thus the energy represented by the motion of its molecules is increased, and risk of condensation and freezing from undue cooling during the expansion of the compressed air while doing work is avoided. In estimating the efficiency of any system of this kind of distributing energy, the energy imparted directly as heat must naturally be taken into account. Another minor use—*e.g.*, in laboratories largely using electrolytic methods—consists in heating thermo-electric batteries by gas jets, and storing the current thus obtained in accumulators. The system is extremely wasteful from the point of view of the output of electrical energy obtained for a given expenditure of chemical energy, but has convenience to recommend it.

GENERATOR GAS.—By this term is meant gas made by the second method defined above—viz., that method by which complete gasification of the fuel is effected. There are three main kinds of generator gas—(1) *producer gas* made by the limited action of air alone on fuel; (2) *water gas* made by the action of steam upon heated fuel; and (3) *semi-water gas* made by the action of both air and steam upon fuel. Gases of the type of water gas and semi-water gas can be made by the action of CO_2, alone or mixed with air, upon fuel.

(1) **Producer Gas.**—The first of these (producer gas) has carbon monoxide as its chief combustible constituent, and its formation depends primarily on the production of carbon monoxide when carbon is burnt in a limited amount of air, the ultimate result being expressed by the reaction—

$$C + \underbrace{O\,(+N_4)}_{\text{Air.}} = CO\,(+N_4).$$

It is usually considered that the production of CO from carbon

* Combustion in an oil engine is also nearly complete, but a good deal of waste is often occasioned by imperfect spraying, oil being ejected in drops with the exhaust.

and a limited supply of oxygen (or air) proceeds in two stages, thus:—

$$(1)\ C + O_2 = CO_2.$$
$$(2)\ CO_2 + C = 2\,CO.$$

According to this view, air on first entering a producer combines with the carbon of the fuel to form CO_2, and this passing up through the mass of hot fuel is reduced to CO, which constitutes the chief combustible constituent of producer gas. It has been recently stated, however, that carbon at a temperature of 1,000°

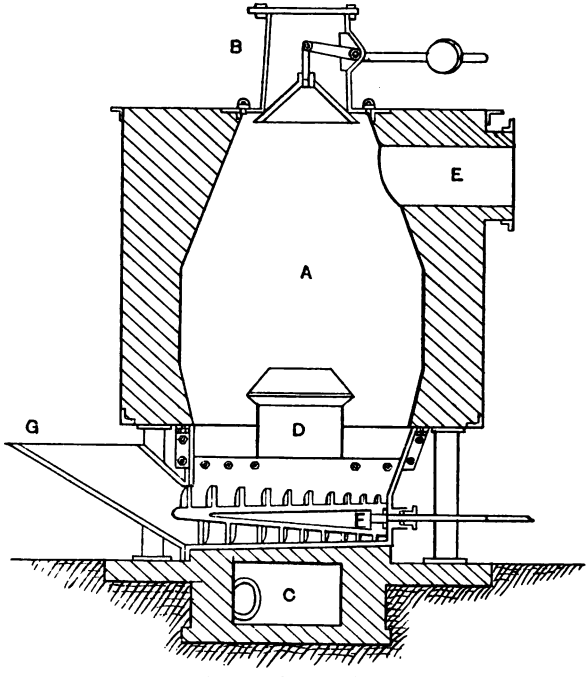


Fig. 7.—Gas producer.

B, Hopper; C, E, flues; D, distributor; F, conveyor; G, shoot.

C. = 1832° F. unites directly with oxygen to form CO, no intermediate formation of CO_2 occurring. Whatever the mechanism of the change the ultimate result is the same—viz., the conversion of solid carbonaceous fuel into the gaseous fuel, CO. The formation of CO by the limited oxidation of C evolves a large quantity of heat, and the main reaction concerned being thus powerfully exothermic, the continuous formation of producer gas without the aid of external heat is easy. A modern form of gas producer is shown in the figure. The producer consists of a combustion

chamber, A, into which the fuel is fed through the hopper, B; it suffers limited combustion by the air entering through the flue, C, and the distributor, D. The producer gas is led off by the flue, E, and the ash and clinker of the gasified fuel are continuously removed by the conveyor, F, which rotates under water, the latter serving to seal the producer chamber. The clinker is forced out at the shoot, G. In general the air is either drawn in by the draught of the stack of the furnace, which is fed by the gas from the producer, or is blown in by injectors.*

As in practice, coal (and not coke) is generally used in a producer, reactions subsidiary to the main chemical change (viz., the production of CO) take place. The mere heat of the combustion chamber suffices to destructively distil a portion of the coal, the residual coke being afterwards gasified by limited combustion. Thus it happens that a certain amount of hydrocarbons appears in ordinary producer gas. The composition of pure producer gas (from carbon only) and that of the ordinary product are given below:—

	Pure Producer Gas.	Actual Sample.
	Per cent.	Per cent.
CO,	34·4	22·8
N,	65·6	63·5
CO_2,	...	3·6
H,	...	2·2
CH_4,	...	7·4
O,	...	0·5
	100·0	100·0

Average producer gas has a calorific value of about 28 Cal. per cubic foot—*i.e.*, about 111 B.T.U. The total amount of chemical energy (as distinct from sensible heat) in the gas thus produced from a given weight of coal is about $\frac{2}{3}$ that in the coal. The fulfilling of the reactions involved in the complete oxidation of C causes the following thermal changes:—

(1) $C + O = CO + 29{,}000$ Cal.
(2) $CO + O = CO_2 + 68{,}000$ Cal.

This means that 12 kilos. of carbon when oxidised to carbon monoxide evolve 29,000 Cal., and when the resulting carbon monoxide is oxidised to carbon dioxide a further evolution of 68,000 Cal. occurs. Therefore, in the preparation of producer gas a large fraction (nearly $\frac{1}{3}$) of the total energy available from the oxidation of the carbon appears as sensible heat in the producer.

* In the particular producer here figured the air is forced in by a steam injector, so that the product is semi-water gas as opposed to pure producer gas (*v.i.*).

Unless, therefore, the producer gas can be used close to the producer, so that it is but little cooled by the time it reaches the point of combustion, a waste of $\frac{1}{3}$ the total energy of the fuel is incurred. The sensible heat of producer gas can, however, be rendered latent and available at a distance in one of several ways, of which the manufacture of semi-water gas serves as a type (*v.i.*).

In all systems of heating by fuel (as opposed to direct electrical heating) great difficulty is experienced in utilising the heat in the products of combustion after their temperature has fallen to a certain minimum. Thus, when there is no feed-water heater (applicable in the case of a boiler) or other economising arrangement, the temperature of the issuing gases may be 600° to 700° F. = 315° to 371° C. The heat thus escaping to the chimney amounts to about 20 per cent. of the whole heat evolved by the combustion of the fuel. It is found to be impracticable in most cases, even when the substance to be heated has to be raised to only a moderate temperature (*e.g.*, the water in a boiler which may have to be heated only to 300° to 400° F. = 149° to 204° C.) to utilise the heat of the products of combustion directly, when their temperature has fallen below 600° F. = 315° C. A certain residuum of heat in the flue gases has to be left to afford a draught, unless some system of forced draught be used. Nevertheless, a large amount of waste occurs in any system of firing in which no special provision exists for turning low temperature heat to account.

Several methods exist of **utilising the low temperature heat** of products of combustion which have accomplished their main work of heating. They differ according to the nature of the industry using the main source of heat. Thus, in industries where evaporation has to be effected, waste gases are made to pass underneath the evaporating pans ; the evaporation of tank liquor in the Leblanc alkali process (*q.v.*, Vol. II.) is a case in point; where moist materials have to be dried, as in drying slurry for cement making, a similar method of economy is practised ; where feed water has to be heated for steam-raising the gases pass through an economiser which consists of a number of vertical iron tubes through which the feed water flows, and round which the boiler gases—*i.e.*, the products of combustion from the boiler grate—circulate. A use of a different kind, specially advantageous when high temperatures have to be produced, consists in heating the air supply before combustion by the waste heat of the furnace gases. Thus, it has been found economical to heat the air supplying a series of boilers by passing it through iron tubes set in the furnace flues, and, therefore, heated by the furnace gases.* This method of pre-heating the materials to be

* Yet another method consists in superheating steam from a boiler on its way to the cylinder by passing it through tubes set in the flues.

burnt is particularly applicable to gaseous firing, as both the fuel and the air can be heated, instead of the air only, as in the case of solid fuel. High temperatures can be easily obtained by employing a system of "regeneration" such as this. A regenerator is shown in the figure, the top portion of which repre-

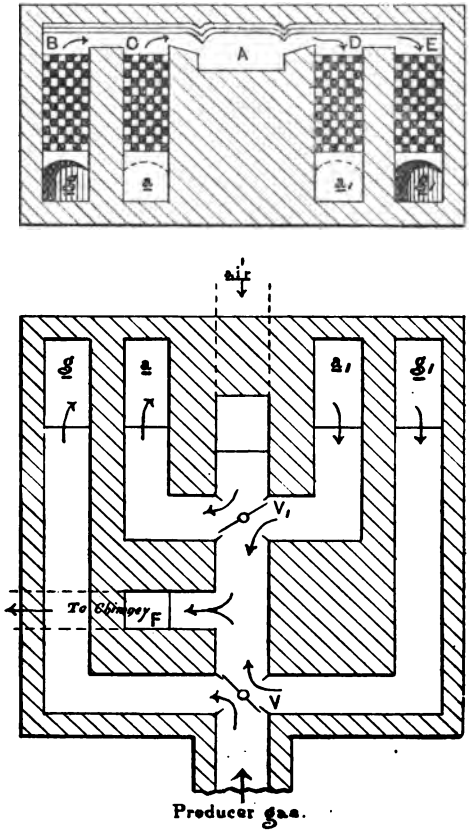


Fig. 8.—Regenerator.

A, Combustion chamber; B, C, D, E, regenerators; *a*, *g*, flues; F, entrance to chimney; V_1, V, valves.

sents a vertical section through a cumbustion chamber, A (in which is the substance to be heated—*e.g.*, steel), and the regenerators B, C, D, E, whilst the lower portion of the figure is a ground plan of the flues through which producer gas and air are fed to the regenerators. The method of operation is as

follows:—When the furnace is at work, the products of combustion leave the combustion chamber, A, by way of the regenerators D, E, which contain chequer work of firebrick to which the hot gases impart a large portion of their heat; they then pass away through the flues, a_1 and g_1 (which are shown in the ground plan in the lower portion of the figure), and thence to the chimney of which the entrance is shown at F. From the same plan it will be seen that the producer gas and the air necessary for its combustion pass through the flues g and a, and thence up the regenerators B and C, shown in the section. When the firebrick in the regenerators D and E has been heated until the temperature of the upper end of the regenerators (nearest the combustion chamber) approaches that of the furnace, the valves V_1 and V are reversed, so that the air and producer gas now flow through the flues, a_1 and g_1, and pass through the chequer work in a direction reverse to that previously taken by the products of combustion, and are thereby heated before they reach the combustion chamber. It is now the turn of the regenerators B and C to become heated by the products of combustion which pass away through the flues, g and a. It will be seen that the whole working is systematic—*i.e.*, the cold gases enter the cooler end of the regenerator and leave at the hot end, whilst the hot products of combustion enter at the warmer end of the regenerator and leave at the cool end. In this case the same canal serves alternately to absorb heat from the products of combustion, and to impart heat to the gases to be burnt; it is obvious that the hot products of combustion and the cold combustible gas (or air) can be passed simultaneously in reverse directions through parallel canals separated by a septum capable of transmitting heat; an arrangement of this sort is shown under the head of destructive distillation of coal (*q.v.*, Vol. II.), and a simple instance thereof is afforded by the regenerative system applied to steam boilers for utilising the heat of their furnace gases, which has been already mentioned (p. 66).

In connection with the loss of energy in furnace gases, attention must be drawn to the fact that the statement frequently made that the escape of much smoke means a large loss of fuel is erroneous. Even dense smoke represents less than 1 per cent. of the total fuel burnt. Bad economy is more often the concomitant of a smokeless chimney, which is frequently an indication of an excessive amount of air above that necessary for combustion, the wastefulness of which has been already pointed out. **Smoke-prevention** being necessary on other than economical grounds, attempts have been made to secure the suppression of smoke, or to remove it from the furnace gases after it has been formed. The former aim is attained (*a*) by the use of non-bituminous fuel; (*b*) by careful stoking at frequent intervals (the destructive distillation of such portion of a heavy charge as

does not immediately ignite being thus avoided); (*c*) by mechanical stokers, which effect the same end (*b*) still better; (*d*) by forced draught (often objectionable on account of the surplus air introduced); and (*e*) by a secondary air supply at a point beyond the main zone of combustion, the hot gases and fresh air being led over a fire-brick bridge or some similar device. Smoke may be removed from furnace gases by washing with a water spray, and many modifications of this method have been devised. It is generally more economical to work a furnace somewhat smokily, and wash the products of combustion free from smoke, than to attempt to prevent the formation of smoke.

Reverting to the subject of regeneration in gaseous firing, it may be said that the regenerator is applicable not only to producer gas, but to the other qualities of gaseous fuel about to be described. The principle in all cases is the utilisation of what would be waste heat for the preliminary heating of the materials about to be burnt.

Since heating by radiation generally results in a more gradual and uniform rise of temperature than heating by contact, methods have been devised for causing a luminous flame to play across the arch (the top of the chamber A, Fig. 8) of a regenerating furnace, so that the material—*e.g.*, plate glass to be softened—may be heated by radiation from the white hot particles of carbon in the flame, and not by contact with the hot gases constituting the flame. Such a luminous flame is obtained by careful adjustment of air and producer gas supplied to the furnace.

2. **Water Gas.**—By this term is meant the gaseous mixture, consisting essentially of CO and H, which is produced by the action of heated carbon upon steam. The reaction appears to take place in two stages, thus—

$$(1)\quad C + 2H_2O = 2H_2 + CO_2.$$
$$(2)\quad C + CO_2 = 2CO.$$

As in the case of producer gas (*v.s.*), it is stated that carbon may be oxidised directly to CO at temperatures above 1,000° C. = 1,832° F., thus—

$$(3)\quad C + H_2O = H_2 + CO.$$

In the case of equation (1) 12 kilos. of carbon in being oxidised by steam require to bring about the reaction an expenditure of 18,200 Cal.; similarly equation (2) requires 39,000 Cal.; equation (3) therefore needs half the sum of these values—viz., 28,600 Cal. In these cases the water is already in the form of steam, but when liquid water is the starting point for calculation, the quantity of heat needed is necessarily greater by the amount necessary to convert the water into steam—*i.e.*, 10,800 Cal. Seeing that the occurrence of the fundamental reaction, $H_2O + C = H_2 + CO$, for the production of water gas involves the absorption of 28,600

Cal. even when the water is already in the form of steam, it is obvious that any system of manufacture must be designed to communicate a large supply of heat to the raw materials, C and H_2O. A plan for supplying this heat, which has the apparent merit of simplicity, would consist in heating a vessel containing solid fuel from without, and blowing steam through it. The method is impracticable on account of the cost of transmitting

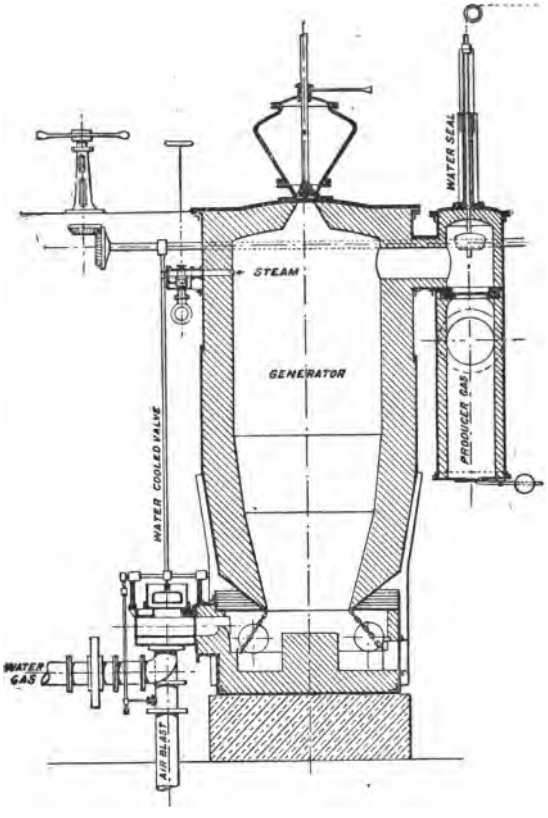


Fig. 9.—Water gas producer.

the heat through the walls of a suitable vessel, such as a gas retort. The device actually adopted consists in obtaining the necessary amount of heat by the oxidation by air of a portion of the fuel which is to be gasified. This is effected by blowing air into the bottom of the generator containing the fuel (as shown in Fig. 9), and thus making producer gas (carbon monoxide and nitrogen), which passes away by the flue on the right of the

figure, heat to the extent of 29,000 Cal. per 12 kilos. of carbon burnt being at the same time evolved. When the interior of the producer is thus highly heated, the air is cut off and steam is blown into the upper part of the generator, forming carbon monoxide and hydrogen, until the heat absorbed by this reaction lowers the temperature below that necessary for its occurrence. The steam passes down the hot column of fuel, its action being thus systematic, and the water gas is lead away through the pipe as shown. The first part of the process. (admission of air) is called the **hot blow,** and the second (injection of steam) the **cold blow.** It will be seen from equation (3) that ideal water gas should contain 50 per cent. H and 50 per cent. CO, (by volume). In practice, however, a certain amount of producer gas, formed during the hot blow, is mixed with the water gas proper resulting from the cold blow. The average composition of water gas is—CO, 41 per cent.; H, 48 per cent.; CO_2, 6 per cent.; N, 5 per cent.—by volume. The producer gas formed during the hot blow has the usual composition (*v.s.*), and is utilised for various heating purposes, such as the "fixing" of hydrocarbons when the primary object of the preparation of water gas is the production of a carburetted gas for enriching common coal gas. Where high temperatures are especially needed, water gas is a better, because more concentrated, fuel than producer gas, but its economical employment depends largely on a use being found for the producer gas which is made as its bye-product. Average water gas has a calorific value of 291 B.T.U. per cubic foot—*i.e.*, 74 Cal. When fuel is gasified by this duplex system, the total quantity of chemical energy in the two gaseous products (producer gas and water gas) amounts to about 77 per cent. of that in the fuel (coal or coke) used.

3. **Semi-water Gas** (Dowson gas).—This form of gaseous fuel is produced by injecting simultaneously air and steam into a producer. The air forms with the fuel producer gas, this process evolving heat; the steam reacts with the fuel to yield water gas, the process absorbing heat. By regulating the proportions of air and steam the temperature of the producer may be kept sensibly constant and a gas obtained consisting of a mixture of producer gas and water gas. The apparatus used for making semi-water gas is simply an ordinary producer, such as is figured in the section on producer gas, provided with a steam injector. It has been indicated above that a common producer only works to advantage when it is situated in close proximity to the furnace which it is supplying, the gas thus reaching the furnace without notable loss of sensible heat. If the connecting pipe be long, much cooling occurs and a large loss results. When instead of the energy appearing as sensible heat in the producer gas, it is converted into potential chemical energy by manufacturing semi-water gas, the distance of the producer from

the furnace is of minor importance. Supposing that the whole of this heat were utilised in the production of water gas, the semi-water gas would contain 58 per cent. of ideal producer gas and 42 per cent. of ideal water gas, and consist of H, 21·1 per cent.; CO, 40·9 per cent.; N, 38 per cent. Semi-water gas as actually made falls considerably short of the ideal composition, containing about H, 17 per cent.; CO, 23 per cent.; CH_4, 2 per cent.; CO_2, 6 per cent.; N, 52 per cent. It has a calorific value of about 36 Cal. or 142 B.T.U. per cubic foot.

Other means than that just described can be used for converting the sensible heat evolved in the formation of producer gas into chemical energy. Thus CO_2 may be substituted for water, its decomposition taking place according to the equation $CO_2 + C = 2CO$, which absorbs for every 12 kilos. of carbon thus gasified 39,000 Cal. The system is used for the preparation of a mixed gas corresponding thermally with semi-water gas, and consisting of a mixture of producer gas with addition of CO (instead of H + CO, as in the case of semi-water gas). Complete utilisation of the heat evolved in the formation of producer gas gives, on this plan, the ideal values—producer gas 65·3 per cent., CO (from CO_2) 34·7 per cent. Such an ideal gas would contain 57·1 per cent. CO and 42·9 per cent. N, and have a calorific value of 48 Cal. per cubic foot. As a supply of pure CO_2 is not available in most places without having recourse to special means of preparation,* this method is reduced in practice to the system of turning back a portion—*e.g.*, one half—of the products of combustion of the furnace fed by the producer, into the producer itself. The CO_2 contained in these products of combustion is converted into CO, and the chemical energy (as distinct from the sensible heat) of the producer gas is thus increased. An advantage of this method is that the CO_2 to be decomposed is already heated, whereas in making semi-water gas an external source of heat is necessary for raising steam. In any ordinary method of working, the sensible heat of the products of combustion is, of course, largely recovered by the use of the regenerator. The disadvantage entailed is the dilution of the gas from the producer with the nitrogen of the products of combustion.

The utilisation of all the foregoing forms of generator gas may be effected in various ways, according as power, heat, or light is required. For mechanical power it may be burnt in a gas engine, the method being especially adapted for use where the demand for power is intermittent, as in electric light stations. Generator gas (usually of the semi-water gas class) is made and stored and drawn upon to supply the gas engines as may be required, thus avoiding the necessity of keeping boilers under steam during a period of the day when the output is small.

* An exception is found in the case of breweries. Lime kiln gases are also fairly rich in CO_2.

The method of using generator gas in a gas engine, differs in no essential respect from that necessary for the employment of coal gas; the smaller volume of air for explosion, and the lower calorific value per cubic foot, being the only conditions of noticeable difference. The use of generator gas for heating has been already mentioned under the description of the production of its various kinds. Its employment for lighting falls into two classes:—(1) Water gas is carburetted with the products of decomposition of petroleum (see *Gas making*, Vol. II.); (2) generator gas, usually water gas, is burnt so as to heat a refractory material and to cause it to emit light. This principle is utilised in the *Welsbach light* in which a "mantle" of refractory material is heated in a non-luminous gas flame (coal gas or water gas); the mantle is made by dipping a knitted cylinder of cotton thread, after it has been washed successively in ammonia and hydrochloric acid, into a solution containing, chiefly, nitrate of thorium, together with nitrates of zirconium, lanthanum, and cerium, and drying at 90° F. = 32° C.* The character of the light varies with the nature of the oxides and the proportions in which they are mixed. The oxides must be as pure as possible, as foreign matter, particularly iron, considerably diminishes the illuminating effect. The gas must be thoroughly burnt lest carbon be deposited on the mantle and destroy it. The Fahnehjelm lighting system is similar in principle; rods of magnesia, set in a metal backing to form a comb, are heated in a water-gas flame and emit a full white light. The magnesia rods gradually shorten and wear away, and have eventually to be renewed. Methods of lighting of this class are economical of gas, a cheap non-illuminating gas, such as water gas, sufficing, and a larger percentage of the total energy of the gas being obtained as light by such means than by the direct burning of illuminating gas. The chief item of cost is the frequent renewal of the refractory material to be heated.

NATURAL GAS is a form of gaseous fuel confined to petroleum districts where it occurs associated with the crude oil. The following analyses show its composition:—

	Per cent.	Per cent.
H, ...	35·9	20·6
CH_4, ...	49·6	72·2
C_2H_6, . . .	12·3	3·6
C_2H_4, . . .	0·6	0·7
CO, ...	0·4	1·0
CO_2, ...	0·4	0·8
O, ...	0·8	1·1

* In modern practice a paste of the oxides is preferred as yielding a more substantial "mantle."

The gas issues at great pressure from the earth (sometimes the pressure is as high as 70 atmospheres). The natural reservoir containing the gas under pressure is tapped (often when sinking a shaft for petroleum) in the manner described in the section on petroleum (*q.v.*), and is conducted by pipe lines to the place of consumption. It is burnt in the way usual for gaseous fuel, and is used for all kinds of manufacturing purposes, its freedom from sulphur giving it a special value for metallurgical purposes. On account of its poverty in heavy hydrocarbons, natural gas has a low illuminating value. The density of an average sample is 0·5 (air = 1), and its calorific value is about 222 Cal. per cubic foot. Besides its main use as fuel, natural gas has another employment—viz., the preparation of the pigment carbon black, which is made by the imperfect combustion of the gas and collection of the resulting soot (see *Pigments*, Vol. II.).

HYDROGEN has but a limited industrial use. Its chief employments are in producing high temperatures by means of the oxyhydrogen blowpipe—*e.g.*, in lead burning and platinum melting—and in filling military balloons. The most convenient method of preparing it consists in acting on zinc with dilute sulphuric acid. The hydrogen from scrap iron and an acid is always contaminated with hydrocarbons and sulphuretted hydrogen, which are generally reckoned objectionable. Cheaper, but less convenient methods, are—(1) heating a mixture of zinc and slaked lime, the reaction being

$$Zn + Ca(OH)_2 = ZnO + CaO + H_2;$$

(2) heating a mixture of anthracite and slaked lime according to the equation

$$C + 2Ca(OH)_2 = CaCO_3 + CaO + 2H_2;$$

(3) heating iron scrap in a current of steam, decomposition taking place as follows—

$$Fe_3 + 4H_2O = Fe_3O_4 + 4H_2.$$

This last reaction can be utilised for obtaining hydrogen by reducing steam by means of semi-water gas, through the action of iron as an intermediary. Steam is first passed over heated iron (as scrap or bar), and hydrogen is produced according to the equation given above. The resulting ferroso-ferric oxide is then reduced by heating it in a current of semi-water gas, and the reduced iron again oxidised by steam, a further quantity of hydrogen being thus obtained. An extremely simple way of obtaining both hydrogen and oxygen consists in decomposing water (slightly acidified to render it conducting) by means of an electric current. The reason why this method has not hitherto been adopted, lies rather in the small demand for hydrogen (not warranting an expensive plant) than in the intrinsic cost of the process. When both anode and cathode are of unattackable material—*e.g.*, platinum—O and H are both obtained, but by

using an oxidisable material at the anode—*e.g.*, zinc—H alone may be prepared, and, in complementary manner, by using a reducible substance such as CuO at the cathode, the H may be suppressed and O alone liberated. Economy may be sometimes secured by such variation of method. Another process of more theoretical and also practical interest is that devised by Mond for separating H from CO in water gas (*v.i.*).

OXYGEN.—This gas is substituted for air when it is required to produce the highest possible temperature by the combustion of a given fuel. The ease with which high temperatures may be obtained by means of oxygen is due to the absence of the diluting effect of the nitrogen with which the oxygen of the air is associated, such nitrogen having to be heated through the same range of temperature as the oxygen and the products of the oxidation of the fuel. Oxygen is especially used when hydrogen is the fuel adopted. It is almost invariably prepared from the air by taking advantage of some reversible reaction. The simplest reaction of this class used for preparing oxygen is that which occurs when barium oxide, BaO, is heated in air to form BaO_2, this product, when raised to a higher temperature, liberating oxygen and becoming reduced again to BaO. As originally carried out on a commercial scale by Brin, barium nitrate is heated in crucibles until its decomposition is complete, and a porous mass of BaO remains. This substance is heated in iron retorts to 600° C. = 1,112° F., and a stream of air, freed from CO_2 by scrubbing in a lime tower followed by one of caustic soda, led over it. Under these conditions BaO_2 is formed, and, on raising the temperature to 850° C. = 1,562° F., is decomposed, giving off oxygen which can be collected and compressed into steel cylinders. According to modern practice the retorts are maintained at a temperature of about 700° C. = 1,292° F., and the pressure varied. During the period when the pressure is about 10 lbs. above that of the atmosphere, oxygen is absorbed, and when the pressure is reduced to about $\frac{1}{15}$ of an atmosphere (absolute)—*i.e.*, a vacuum of about 28 inches—oxygen is given off, the process thus resolving itself into alternately pumping air into the retorts, and exhausting oxygen from them. By this process only about 8 per cent. of the oxygen which a given weight of BaO is capable of absorbing in the formation of BaO_2 and subsequently giving up, is obtained in each operation; but the comparative rapidity of the alternate stages of the process, and the diminished wear and tear of the retorts, which are kept at a fairly constant temperature, more than compensate for this drawback. The oxygen always contains some nitrogen—*e.g.*, 10 per cent.—and thus is unsuitable for such purposes as require the highest temperature of the oxyhydrogen blowpipe.

Another method of the same class consists in heating manganese dioxide with caustic soda in presence of air, whereby sodium

manganate and steam are produced in accordance with the equation—

$$MnO_2 + 2NaOH + O = Na_2MnO_4 + H_2O.$$

The sodium manganate is then heated in a current of steam, and Mn_2O_3, caustic soda, and oxygen are produced, thus—

$$2Na_2MnO_4 + 2H_2O = Mn_2O_3 + 4NaOH + O_3.$$

When the oxygen has been collected, the mixture of Mn_2O_3 and NaOH may be again heated in air, and this last equation becomes reversed. Thus by heating a mixture of caustic soda and oxide of manganese in air and in steam alternately, a supply of oxygen can be obtained from the air.

A third reaction, greatly resembling the last, is that obtained by heating calcium carbonate and lead oxide in a stream of air (Kassner's process). The lead oxide is oxidised, calcium plumbate being produced according to the equation—

$$2CaCO_3 + PbO + O = 2CaO . PbO_2 + 2CO_2.$$

The resulting calcium plumbate is moistened and treated with furnace gases at a temperature below 100° C. = 212° F. The CO_2 of the furnace gases attacks the plumbate forming PbO_2 and $CaCO_3$. The mixture is then heated in a retort, whereby the lead peroxide is decomposed, and oxygen given off, its evolution being aided by injecting steam. On raising the temperature of the retort, the $CaCO_3$ is also decomposed, yielding CO_2 (which is used in the first stage of the process in the next cycle of operations), and a mixture of PbO and CaO is obtained, which on heating in air again yields $2CaO . PbO_2$, capable of undergoing the same series of changes.

Besides these purely chemical methods, a process based on the difference in solubility in water of oxygen and nitrogen—the former being nearly twice as soluble as the latter—has been proposed for the commercial preparation of oxygen. By alternately compressing air over water, and then drawing off the dissolved gases from the water by creating a vacuum over its surface, a progressive enrichment in oxygen of the resulting mixture of gases takes place, until after eight absorptions and exhaustions a mixture containing 97·3 per cent. of O and 2·7 per cent. of N is produced.

Another method of separation not depending on definite chemical reactions is that which takes advantage of the property of an indiarubber membrane of allowing a readier passage of oxygen than of nitrogen, the process being known as dialysis. It is carried out by maintaining a vacuum inside a bag made of thin indiarubber, the air pumped out being found to be richer in oxygen than is atmospheric air. By repeating the process, approximately pure oxygen can be produced. The method in no way depends on the property of diffusion. The electrolytic

preparation of oxygen may be effected simultaneously with that of hydrogen (*v.s.*). No practical outcome of these methods has hitherto taken place.

HEATING BY MEANS OF ELECTRICAL ENERGY.—Seeing that at present by far the larger part of electrical energy industrially employed is obtained by the combustion of fuel, the reconversion of electrical energy into heat is in most cases too costly and wasteful to be of practical importance. In special cases, however, where nicety of application, or extreme localisation of the heating effect, or the absence of the products of common combustion, is of greater moment than is the cost of the proceeding, electrical heating may be usefully employed. Such minor applications as in cooking and surgery can scarcely be here considered, but the use of electrical energy for the production of heat in chemical and metallurgical processes may be noticed.

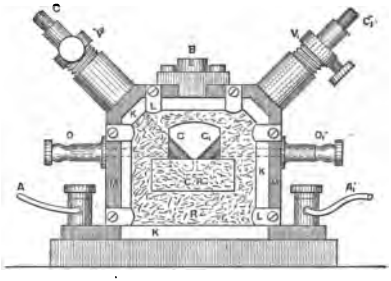


Fig. 10.—Electric furnace.

K, Metallic framing; R, refractory material; C R, crucible; M, metal castings; A, terminal; V, carbon holder; L, plates holding mica sheets; O, gas tubes.

The accompanying figure exhibits the typical arrangement of an electric furnace, whether used for laboratory purposes or for a manufacturing process. Essentially it consists of a box of refractory material, K, R, into which protrude two electrodes (usually of carbon), C, for the conveyance of the current to the interior of the furnace charge. Sight-holes covered with mica and tubes for the inlet and outlet of any desired gas are provided. The operation of the furnace depends upon the conversion of electrical into heat energy when the current is caused to traverse a considerable resistance. An actual arc may form, or contact between the electrodes may be secured by the insertion of a conductor of high resistance, such as a slender carbon rod, or the furnace charge itself may perform the like function. The temperature that can be attained in this manner approximates to that of the electric arc, which may be taken as identical with the boiling point of carbon, roughly estimated at 3,500° C. = 6,322° F. The effects that can be produced at such a tempera-

ture at present belong to the province of pure chemistry. The only industrial applications of the electric furnace which have attained any appreciable degree of success, are in the smelting of aluminium bronze (*q.v.*) and in the manufacture of phosphorus (*q.v.*). The fundamental advantage obtained by means of the electric furnace is the facility with which any material can be heated without contact with the products of combustion. When such heating is performed by means of an ordinary furnace, the whole of the energy has to be transmitted through the walls of a retort or corresponding vessel, this transmission occasioning great waste of heat and the rapid destruction of the enveloping vessel. The chief drawback to the use of the electric furnace arises from the difficulty of distributing the heat generated over the whole mass of the charge, the size of the charge that can be handled in each furnace being thereby seriously restricted. Possible use for the electric furnace consists in the manufacture of products not obtainable at temperatures that can be reached by any other means. Thus *silicon carbide*, SiC, has been synthesised in the electric furnace by reducing quartz with carbon, and has been found commercially useful as as abrasive material in place of emery. *Calcium carbide*, CaC_2, is prepared by heating a mixture of powdered lime and breeze (coal dust) in the electric furnace; reference to its use as a source of acetylene will be found in the section dealing with coal gas.

MEASUREMENT OF TEMPERATURE.—The fact that two quantities of fuel yield the same quantity of energy on combustion, does not imply that the energy they yield is of the same intensity—that is, that the heat produced is at the same temperature. It is obvious that the larger the quantity of heat evolved by the combustion of a given weight of fuel and the smaller the weight of the products of combustion and ash, the higher will be the temperature of the burning mass and of its products and ash. When the weight and the specific heat* of the products of combustion are known, it is possible to calculate the maximum temperature which could be produced by the combustion of the fuel, when no limiting factor is active. In the case of fuel burning in oxygen free from a diluting gas—*e.g.*, nitrogen—the calculated temperature is considerably higher than that of the dissociation of the chief products of combustion, CO_2 and H_2O; when nitrogen is present (as when air is used) the diluting effect of the inert gas is sufficiently great to lower the calculated temperature to about the dissociation temperature. It is probable that at industrial high temperatures a portion of the gaseous products of combustion is, for a period at least, in a state of dissociation. Owing to the facts that the specific heats at high temperatures of the products of combustion of fuel are not accu-

* This being, of course, taken at the temperatures concerned, at which it is considerably higher than at ordinary temperatures.

rately known, that the amount of dissociation is also uncertain, and that loss by conduction and radiation greatly increase with rise of temperature, the calculation of the maximum temperature that shall be produced by a given fuel is futile. Direct measurement is therefore necessary.

METHODS FOR MEASURING TEMPERATURE may be classified as follows:—

1. Measurement of alteration in volume of bodies.
2. Observation of change of state of substances.
3. Measurement by the colour of light emitted.
4. Measurement of alteration in electrical resistance.
5. Measurement of the E.M.F. of a thermo-electric couple.
6. Calorimetric measurement.

1. Taking these in order, the first is the method most frequently used, and is that exemplified by the common thermometer, a description of which is here unnecessary. An ordinary thermometer, filled with mercury and having only mercury vapour in the space above the mercury column, is fairly reliable up to 300° C. = 572° F.; but if higher temperatures are required, the space above the column must be filled with some inert gas, the pressure of which will raise the boiling point of the mercury. Thus, nitrogen-filled thermometers may be used up to about 400° C. = 752° F., and thermometers containing CO_2 at a pressure of 20 atmospheres to 550° C. = 1,022° F. An alloy of sodium and potassium, liquid at the ordinary temperature, has also been used, on account of its high boiling point, for thermometers up to about 500° C. = 932° F. The accuracy of a thermometer is much influenced by the character of the glass used in its construction. Ordinary glass contracts slowly after having been blown into bulb form, thus causing a rise in the reading of the thermometer. Preparation of the bulb years before use decreases this defect. Special glass, prepared at Jena, for which freedom from this tendency is claimed, has one of the two following compositions:—

	I.	II.
SiO_2	67·5	52·0
Al_2O_3	2·5	...
CaO	7·0	...
ZnO	7·0	30·0
Na_2O	14·0	...
K_2O	...	9·0
B_2O_3	2·0	9·0

Alcohol thermometers are made for low temperatures, but the dilatation of alcohol is by no means as regular as that of mercury.

The methods of measuring temperature which depend upon

the expansion of solids by heat have but little application, as expansion of most solids is small and irregular, needing multiplication and correction before it can be utilised for measuring temperature. Moreover, when used at high temperatures, most solids are apt to take a permanent set, impairing subsequent observations, unless they are frequently recalibrated. An alteration of volume by rise of temperature—not due to separation of molecules, but arising from increase of aggregation by incipient sintering, and amounting, therefore, to a contraction instead of an expansion—has been used in the clay industries for roughly estimating the temperature of kilns. The method, which consists in observing the shrinkage of a test piece of plastic clay (see *Clay Industries*, Vol. II.), was originated by Wedgwood; the clay test piece is measured, after exposure in the furnace, by dropping it into a wedge-shaped groove.

Since the expansion of gases, the critical temperatures of which are much below the ordinary temperature of the air, is for ordinary high temperatures approximately regular for a given increment of temperature (viz., $\frac{1}{273}$ of the volume of the gas at 0° C. for each degree C.), such gases (*e.g.*, air and hydrogen) may be employed for measuring temperatures by their expansion. The apparatus necessary consists essentially of a bulb of glass, porcelain, or platinum, of known volume, which is attached to a capillary tube, serving to make connection with the measuring part of the apparatus. This bulb is inserted into the space the temperature of which is to be measured, the capillary tube protruding for observation. The known volume of gas in a gas thermometer may be allowed to vary, and its increase of volume be measured at constant pressure, or, conversely, the volume may be kept constant and the pressure requisite for this may be measured. Certain objections arise to either of these plans singly. Thus, in the first case, when the gas is allowed to expand under constant pressure, a portion of it is expelled from the bulb into the measuring part of the apparatus (consisting essentially of an index of liquid in a graduated tube); this portion is no longer subjected to the temperature to be measured, so that as the temperature rises, a continually decreasing quantity of gas is being caused to expand in the bulb of the thermometer, necessitating a correction; consequently the delicacy of the instrument decreases with rise of temperature (since the fraction $\frac{1}{273}$ is referred to the volume at 0° C.). In the second case, where the volume of the gas is kept constant, this objection does not arise, but on the other hand, a moderate rise of temperature—*e.g.*, from 0° to 273° C. = 32° to 523° F.—means a large increase of pressure on the bulb, such as one atmosphere in the case quoted. The considerable pressure thus caused at high temperatures becomes serious when the material of the bulb reaches its point of plasticity. To overcome these objections

a pyrometer has been devised by Wiborgh (*Journ. Soc. Chem. Ind.*, 1889, 214), the principle of which is as follows:—A porcelain bulb, connected by a capillary tube to a manometer, is exposed to the temperature to be measured. The gas within it is allowed to expand and escape until the temperature of the bulb has reached that of the furnace in which the apparatus is used. A measured volume of gas, representing a known fraction of the volume of the gas in the pyrometer bulb, and being at a known temperature lower than that of the bulb (*e.g.*, the temperature of the outer air), is then forced into the heated bulb, and the expansion consequent on the rise of temperature of this air is measured by the pressure required to balance it; this pressure is obtained by raising the mercury in the manometer tube, and gives the necessary data for calculating the temperature of the main bulb of the apparatus. The following expression will represent the application of the data:—

$$V = H\frac{V + V_1\left(\frac{T + 273}{t + 273}\right)}{H + h}$$

T is the temperature to be measured, t that of the portion of air forced into the bulb, V the volume of the bulb, V_1 the volume of the air forced in, H the pressure of the atmosphere at the time of observation, and h the pressure required to balance that of the air which has been forced in, after it has expanded.

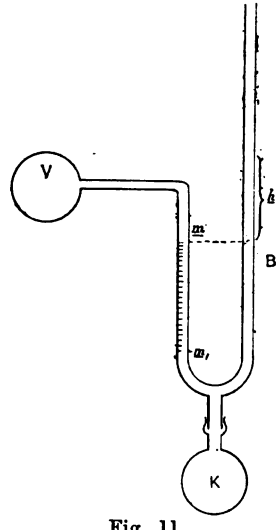


Fig. 11.
Wiborgh's Pyrometer.
V, Bulb; B, manometer; $m_1 - m$, volume of injected gas; h, height of mercury; K, rubber ball.

The apparatus necessary is represented diagrammatically by the accompanying figure, in which V is the bulb of the instrument, B the manometer tube, $m_1 - m$ the volume of gas driven in, and h the height of the column of mercury in the manometer balancing the increase of pressure. K is a collapsible rubber ball serving to inject the gas and to adjust the manometer level.

By such an arrangement the objections that are valid against the two types of gas pyrometers described above are avoided. For although during the measurement the volume of heated gas is kept constant, the increment of pressure to be measured is not large, depending, as it does, on the volume of the small quantity of air introduced before each measurement.

Gas thermometers are available through a large range of tem-

perature, serving both as low temperature thermometers and as **pyrometers**, a term applied to thermometers for measuring high temperatures. An alternative method of applying the expansion of a gas for the determination of temperature, which requires no special apparatus, consists in heating a refractory vessel of known volume, containing hydrogen, to the temperature to be measured, sealing the exit end of the vessel, and ascertaining the quantity of hydrogen remaining in the vessel; this determination may be effected either gravimetrically by oxidation and weighing as water, or volumetrically by sweeping it out with a current of HCl and measuring it over water (in which HCl is soluble).

In yet another method, which can be made continuous in operation and capable of indicating results at a distance from the furnace, air, heated to the temperature to be measured, is passed through a small orifice, cooled to a known temperature, and then passed through another small orifice of the same dimensions as the first. The volume of the air passing both orifices is the same at the orifices, but within the intermediate space it undergoes a contraction registered by an alteration of the pressure which the air exerts. This pressure is indicated on a manometer, if necessary at a distance.

2. This method depends upon the fact that the change of state of a pure substance occurs at a constant temperature when the pressure is constant. It usually consists in observing the behaviour of substances of known melting point or boiling point, when a test piece of the substance is exposed to the temperature to be measured. An example of the method is given in the section on *Clay Industries*, Vol. II., under the head of *Seger's Normal Cones*. Alloys of silver, gold, and platinum of known melting point are also sometimes used.

The following figures constitute a fair range of temperatures which can be determined in this way :—

		Cent.	Fahr.
Lead,	m.p.,	325° =	617°
Mercury,	b.p.,	358° =	676°
Zinc,	m.p.,	412° =	774°
Sulphur,	b.p.,	444° =	831°
Boric anhydride,	m.p.,	577° =	1,071°
Potassium iodide,	m.p.,	634° =	1,173°
,, bromide,	m.p.,	699° =	1,290°
,, chloride,	m.p.,	734° =	1,353°
Sodium chloride,	m.p.,	772° =	1,421°
,, sulphate,	m.p.,	883° =	1,621°
Zinc,	b.p. (circ.),	934° =	1,713°
Silver,	m.p.,	961° =	1,762°
Gold,	m.p.,	1,062° =	1,944°
Potassium sulphate,	m.p.,	1,066° =	1,951°
Copper,	m.p.,	1,080° =	1,976°
Palladium,	m.p.,	1,500° =	2,732°
Platinum,	m.p.,	1,775° =	3,227°
Iridium,	m.p.,	1,950° =	3,542°
Carbon,	m.p. (circ.),	3,500° =	6,332°

3. The measurement of temperatures by estimating the light emitted by incandescent bodies has a certain limited application. A rough estimation of temperature by the eye has long been in use in the arts; thus the following technically named temperatures correspond approximately with the measured temperatures given below :—

	Cent.	Fahr.
Dull red,	525° =	977°
Cherry red,	800° =	1,472°
Deep orange,	1,100° =	2,012°
White,	1,300° =	2,372°
Dazzling white,	1,500° =	2,732°

Judgment of such temperatures can be aided by a simple optical device. The heated object is viewed through a Nicol's prism, and the ray of light thus polarised is then caused to traverse a quartz plate which rotates the plane of polarisation through an angle proportional to the thickness of the quartz and approximately inversely proportional to the wave length of the light (which of course determines its colour, and varies with the temperature of the luminous object). The ray then passes through a second Nicol's prism which serves as an analyser, and is rotated until extinction of the beam is attained as nearly as possible, the red being generally the light chosen for extinction. The angle of rotation serves as a measure of the predominant wave length of the light from the incandescent substance, and, therefore, serves to judge its colour, and hence its temperature. The method is chiefly useful in checking fluctuations of temperature in industrial furnaces.

4. The electrical resistance of a pure metal increases with the temperature, a fact which has been utilised for the determination of temperatures by measuring the resistance of a platinum wire exposed to the temperature to be ascertained. A recent form of instrument consists of a thin platinum wire coiled in a tube of refractory material, and insulated by a mica plate on which it is wound, the two ends being welded on to thick platinum leads, thus :—

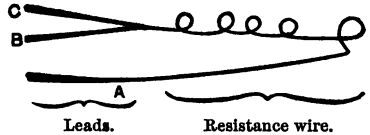


Fig. 12.

The object of one of the leads being doubled is to enable the measurement of the resistance of the leads (which, of course, varies with their temperature, in its turn varying with the temperature of the coil), as distinct from the resistance coil, to be made. It will be obvious that if the leads A and B be attached

to the resistance box (for the principles upon which the measurement of electrical resistance is based, consult an electrical text book), the resistance of these leads and the coil can be measured. On connecting B and C with the resistance box, instead of A and B, the resistance of the circuit represented by B and C is thus measured, and since all three leads are made of the same dimensions and are exposed to the same temperature, this latter measurement allows of the correction of the first measurement for the resistance of A and B. Measuring a temperature by this instrument resolves itself into taking the resistance of the platinum coil plus that of the leads, and deducting the resistance of the leads, when the tube containing the coil and as much of the leads as is necessary are exposed to the temperature to be measured. In practice various minor corrections are necessary for obtaining accurate results. The alteration of the specific resistance of pure platinum with rise of temperature being known, the resistance of the coil can be determined at a known ordinary temperature—*e.g.*, 15° C. = 59° F.,—and high temperatures measured without further calibration.

5. When a junction of two dissimilar metals is heated to a temperature above that of their remote ends, an electrical current is generated in any circuit connecting them, the E.M.F. of which is proportional to the difference of temperature between the heated junction and the portions of the metal pieces which are kept cool. The measurement of the E.M.F. will therefore serve as a measurement of this difference of temperature. This principle has long been used in the case of the *thermopile*, which consists of several such thermo-electric couples arranged so that one set of junctions to be heated may be exposed to the source of heat the temperature of which is to be measured, the other set being allowed to remain cold, or intentionally kept so. The older forms of thermopile were made of metals giving an E.M.F. relatively considerable—*e.g.*, bismuth and antimony. The fusibility of these substances prevented their application to the measurement of high temperatures. Lately, a couple consisting of platinum and an alloy of platinum with 10 per cent. of rhodium, has been used in pyrometry. The couple is exposed to the temperature to be measured and the current generated is passed through a high resistance reflecting galvanometer, the deflections of which are proportional to the E.M.F. of the current (on account of the high resistance of the circuit), and therefore to the temperature to which the couple is exposed. The instrument is calibrated by immersing the junction in substances of known fusing point. A continuous record of the indications given by the galvanometer can be obtained photographically.

The instrument has been found of practical utility for such purposes as the determination of the temperature of the hot blast from Cowper's stove (see *Iron*).

6. A method differing essentially from any of the foregoing is the calorimetric method, in which a given weight of a substance of known specific heat is raised in temperature to that to be measured, and then cooled by immersion in a known weight of water, the rise of temperature of which is ascertained. The most suitable substance for this purpose is platinum, the specific heat of which is known with fair accuracy between 0° C. and 1,200° C. = 32° and 2,192° F., being 0·03350 at the former temperature and 0·03818 at the latter. This method is naturally discontinuous unless several apparatus be employed in succession.

A modification consists in the use of a stream of water of known temperature circulating through a copper tube coiled in the space the temperature of which is to be determined. By a knowledge of the quantity of water flowing, of the difference of its temperature at influx and efflux, and of the specific heat of water, the number of calories imparted through the copper tube can be ascertained. This can be translated into temperature after the indications of the instrument have been standardised by observing its readings in a furnace the temperature of which is gauged by its ability to fuse substances of known melting point. A variation of this method, especially applicable to hot blast stoves, consists in diluting the hot blast with a known proportion of cool air of known temperature and reading the temperature of the mixture.

Since modern methods of pyrometry, especially the use of the thermo-electric apparatus, have been available, it has been found that most industrial temperatures are lower than was formerly supposed. The following are given on the authority of Le Chatelier :—

	Cent.	Fahr.
Melting point of grey cast iron,	1,220°	= 2,228°
,, ,, ingot iron (C = 0·1 per cent.),	1,475°	= 2,687°
,, ,, hard steel (C = 0·9 ,,),	1,410°	= 2,570°
Bessemer converter (at finish),	1,580°	= 2,876°
Open hearth steel furnace (at tapping),	1,580°	= 2,876°
Crucible steel furnace,	1,600°	= 2,912°
Puddling (temperature of bloom),	1,330°	= 2,426°
Blast furnace (in front of twyer),	1,930°	= 3,506°
Crucible glass furnace,	1,375°	= 2,507°
Siemens' tank glass furnace,	1,400°	= 2,552°
Hard porcelain furnace,	1,370°	= 2,498°
Incandescent lamp filament,	1,800° to 2,100°	= 3,272° to 3,812°.

DIRECT CONVERSION OF CHEMICAL ENERGY INTO ELECTRICAL ENERGY.—Certain chemical reactions, capable of causing evolution of heat, can be made to take place under such conditions that a portion of the heat appears as electrical energy. Thus, when 65 grams of zinc are dissolved in dilute sulphuric acid under ordinary conditions 37 Cal. are evolved, and no current which can be utilised is generated. When, however,

zinc is allowed to dissolve in a cell containing a piece of platinum,* and is connected with this platinum by an external wire, a smaller quantity of heat is evolved in the cell, and the balance of the energy represented by the 37 Cal. due to the dissolution of the zinc appears as electrical energy in the wire. That fraction of the chemical energy liberated by the dissolution of the zinc which appears as electrical energy varies according to the nature of the substance used as the opposing electrode. When this substance is chemically inert, as are platinum and carbon for instance, the fraction of energy converted into electrical energy is large, the reverse being true when the substance forming the opposing electrode is comparatively active—*e.g.*, copper. Since the action of a simple cell causes a film of hydrogen to be deposited on the plate opposing the zinc, this plate becomes, to all intents and purposes, equivalent to one of hydrogen, a substance less inert than the subjacent material. The fraction of chemical energy converted into electrical energy by a cell having a plate thus "polarised" by a film of hydrogen is smaller than that proper to the couple originally composing the cell. Mechanical devices, such as roughening the platinum, and thus preventing the attachment of hydrogen, are moderately effective in mitigating this drawback.

A given quantity of zinc, dissolving under such conditions that it generates a current of electricity, always produces the same quantity of electricity, but the pressure at which this quantity is delivered varies according to the nature of the electrode opposing the zinc, an unattackable electrode giving a higher electrical pressure (E.M.F.) than one susceptible of attack. It must be remembered that electrical energy is the product of a quantity of electricity into electrical pressure (quantity × E.M.F.). Whence it follows that as the quantity is constant for the dissolution of a given weight of zinc, the corresponding amount of electrical energy produced varies directly with the E.M.F. of the couple (zinc and the opposing electrode).

The dissolution of zinc in dilute sulphuric consists, in effect, in the oxidation of zinc accompanied by the reduction of water with liberation of hydrogen. For simplicity's sake, the small energy changes due to the subsequent formation of zinc sulphate need not be considered here. The energy available for conversion into electrical energy in a simple cell, in which zinc is thus dissolved, is, therefore, measured by the difference between the heat of formation of ZnO and of H_2O † (85·8 – 68·4 = 17·4 Cal.). It is plain that if the hydrogen can be prevented from escaping free from an electrical cell, but, on the contrary, is burnt in the cell, the minus quantity in the above

* Which should be platinised to facilitate, by the roughness of the surface, the escape of hydrogen due to the dissolution of the zinc.

† Molecular quantities, expressed in grams.

equation is reduced or eliminated. This condition is secured by the use of compound cells, in which the hydrogen that would otherwise appear at the electrode opposed to the zinc is suppressed thereat by a suitable oxidant. Such a suppression of hydrogen not only yields a larger fraction of the chemical energy as electrical energy, but obviates the necessity for preventing polarisation of the electrode opposing the zinc by means of mechanical roughening of the plate, for depolarisation is effected *pari passu* with the suppression of the hydrogen.

The **Daniell's cell** is a typical compound cell. It consists of zinc in zinc sulphate or dilute sulphuric acid, and copper in copper sulphate, the two liquids being separated by a porous pot. The fundamental chemical changes consist in the dissolution of zinc in the form of sulphate in one compartment, and the deposition of copper from the sulphate, in the metallic state in the other compartment; the balance of chemical energy capable of conversion into electrical energy is represented by the difference between the heats of formation of $ZnSO_4$ and $CuSO_4$,* in solution —that is, 248·5 - 198·4 = 50·1 Cal. In this case the hydrogen is suppressed by the action of the copper sulphate in the copper compartment of the cell, and its equivalent of copper is precipitated upon the copper electrode; the whole of the energy represented by the hydrogen is, therefore, not utilised, as copper is reduced in its place. For a cell thus working, with elimination of copper instead of hydrogen, the Daniell's cell is remarkably efficient, inasmuch as the quantity of electricity corresponding with the dissolution of a given weight of zinc is delivered by this cell at the maximum possible E.M.F.

Since the chemical energy of a Daniell's cell is equivalent to 50·1 Cal. for the dissolution of 65 grams of zinc, and since 1 unit of electrical energy (1 unit of quantity × 1 unit of pressure) is equal to 0·241 gram unit of heat, the electrical energy corresponding with the chemical energy of a Daniell cell is

$$\frac{50{\cdot}1 \times 1000}{0{\cdot}241} = 207{,}900 \text{ (nearly) electrical units of energy.}$$

Seeing that 1 gram equivalent (32·5 grams) of zinc, in accordance with Faraday's law, corresponds with 96,540 units of electrical quantity (coulombs), the E.M.F. at which this electrical quantity must be delivered in order to be equal to the total electrical energy is

$$\frac{207{,}900}{96{,}540 \times 2} = 1{\cdot}07 \text{ units of electrical pressure, that is, volts.}$$

Other forms of compound cells are used in which zinc is the metal attacked, and thus employed as a source of energy, whilst the opposing electrode may be composed of various materials, and be immersed in several distinct **depolarisers**. Thus, the **Grove cell** consists of a plate of zinc immersed in dilute sul-

* Molecular quantities, expressed in grams.

phuric acid and one of platinum immersed in strong nitric acid, the two liquids being separated by a porous cell. The **Bunsen cell** is identical with the Grove, save that retort-carbon is substituted for platinum. In both cases the hydrogen that tends to appear at the unattacked electrode is oxidised by nitric acid, and serves as a direct source of increased E.M.F. in the manner described above; since, however, the reaction causing the oxidation of the hydrogen involves separation of no substance possessing (as does the copper in the Daniell cell) any considerable amount of chemical energy, a larger E.M.F. (1·9 to 2 volts) is obtained, and a more complete conversion of the chemical energy of the zinc into electrical energy is secured.

Other materials that are unattacked by strong nitric acid—*e.g.*, iron and aluminium—may be substituted for carbon or platinum, but are generally less convenient and reliable.

Chromic acid is sometimes used as a depolariser and as an oxidant for the hydrogen, and has the advantage of being available in a simple cell, because unlike nitric acid, it has no violent action on zinc and can be allowed direct contact with this metal as well as with the opposing plate, usually carbon; thus a **bichromate cell** in its simple form consists merely of a zinc plate and one of carbon immersed in a solution of chromic acid, to which has been added sulphuric or hydrochloric acid. An E.M.F. of about 2 volts is thus obtained, and the internal resistance of the cell may be made very low, as no septum is requisite. When the battery is to be continuously used a porous pot surrounding the carbon and containing chromic acid solution is an advantage, the zinc in this case being immersed in dilute hydrochloric acid. The oxidation of hydrogen by chromic acid results in the formation of chromic sulphate when sulphuric acid is present, and chromic chloride when hydrochloric acid is used. In the former case, should bichromate of potash have been taken as the source of chromic acid, hard crystals of chrome alum ($KCr(SO_4)_2.12H_2O$) are formed and adhere to the plates, impeding the action of the battery. The use of chromic acid, or of hydrochloric acid in place of sulphuric acid, is therefore preferable.

A form of cell in which a **solid depolariser** is used is the **Leclanché**, which consists of zinc immersed in a solution of ammonium chloride, and carbon, surrounded with fragments of manganese dioxide, in the same solution. The function of the manganese dioxide is to oxidise the hydrogen which would otherwise appear at the carbon; the lower oxide of manganese thus produced is re-oxidised by atmospheric oxygen, which thus becomes the true depolariser. The fact that the Leclanché cell, when used for a considerable output of current, speedily becomes exhausted and recovers its efficiency on standing, lends support to this view of the action of the manganese dioxide.

The chemical reaction concerned in the dissolution of zinc in ammonium chloride results in the formation of zinc chloride, ammonia, and hydrogen. The last named is oxidised as stated above, whilst the ammonia and zinc chloride when present in considerable quantity, as in an exhausted battery solution, combine to form the compound $ZnCl_2.NH_3.Aq$, which separates in needle-shaped crystals. The E.M.F. of a Leclanché cell is about 1·4 volts.

Zinc is sometimes used in alkaline exciting liquids, this plan being feasible on account of the solubility of zinc oxide in caustic alkalies. A cell of this type is formed by zinc in caustic soda and carbon in the same liquid, the depolariser being cupric oxide, which is reduced to metallic copper. The E.M.F. is comparatively low—under 1 volt.

Whenever zinc is used in a galvanic cell, excited by an acid liquid, it is economical to amalgamate the zinc—that is, to coat it with mercury. The reason for this treatment is that commercial zinc contains impurities, notably lead, which are electronegative to it, and with it form local couples which cause the dissolution of the zinc without contributing to the main output of electricity. The action of the mercury appears to be to dissolve the surface layer of the zinc, and thus to render all parts uniform in texture and composition. The difference in behaviour between amalgamated zinc and zinc not thus treated, is shown by the fact that when immersed alone in dilute sulphuric acid the amalgamated zinc is not perceptibly attacked, whereas the unamalgamated metal is freely dissolved.

In a properly arranged cell the chemical energy of zinc can be almost completely converted into electrical energy, but the money cost of the zinc, together with that of the necessary exciting and depolarising liquids, is prohibitory of its employment as a source of energy on a commercial scale.

A comparison of the energy available for mechanical work obtained by burning zinc in a galvanic cell and carbon beneath a boiler, gives the following results:—65 grams of zinc used in a Daniell's cell (which would probably cost least, of all known combinations, for depolarising solutions) will give electrical energy equal to 50·1 Cal.* This is convertible, with a loss not exceeding 10 per cent., into mechanical work by the use of an electric motor, the final output being, therefore, an amount of mechanical work equal to 45·1 Cal. The same weight of carbon will give 520 Cal. when burnt; about 10 per cent. of this energy —that is, 52 Cal.—is convertible into mechanical work through the medium of a boiler and steam engine. From this it will be

* If oxidised directly without causing the reduction of an equivalent of copper, an increased output—viz., 85 Cal. (Zn,O = 85 Cal.)—would be obtained, but no cell is known which is capable of using air as a depolariser for continuous working.

seen that, even were the cost of carbon and zinc per unit weight identical, the balance of advantage would be on the side of the carbon; as a fact, the cost of zinc is about fifty times that of carbon in the form of coal, a relation which shows that the commercial adoption of zinc as a source of energy is impracticable.*

Attempts to utilise the chemical energy of iron for the direct production of electrical energy have led to but little result, on account of the impossibility of amalgamating iron and the consequent uncontrollable rate of dissolution in acid which occurs when iron is used as the attackable plate of the cell.

Aluminium, when used as a source of electrical energy, has the advantage of a high heat of oxidation, a high valency, and low atomic weight (involving a large output of energy for a small weight of metal), and a low specific gravity. It is difficult of application, because when amalgamated its rate of dissolution is increased instead of being controlled.

There is no inherent reason why the chemical energy evolved by the oxidation of carbon should not be directly converted into electrical energy. If this could be done with even moderate success, a higher output of mechanical work than the 10 per cent. now commonly obtained from the combustion of coal, could be readily achieved, for the use of an electric motor allows of an output of about 90 per cent. of the energy supplied to it. Attempts in this direction have already been made. The type of apparatus used consists of a carbon plate immersed in fused sodium nitrate, opposed to an iron plate in the same liquid. Under these conditions the carbon is oxidised at the expense of the nitrate, whilst the iron is only superficially attacked. An output of about 30 per cent. of the calculated possible quantity of electrical energy has been thus obtained. The chief difficulties in utilising such an arrangement are the irregular oxidation and disintegration of the carbon. It is obvious that the nitrate is used pending the achievement of success in employing the oxygen of the air as an oxidant for the carbon; the cost of the process is much enhanced by this use of a comparatively expensive form of oxygen.

A **secondary cell** is one which can be regenerated, after it has furnished its full output of current, by the passage of a current from an external source in the reverse direction to the original current; the original condition of the plates is thus restored, and the cell made fit for a further output; such a cell can be used for the storage of electrical energy **(storage cell).**

Any one of the **primary cells**, such as have been described above, if depending for its action upon chemical changes which

* Since the product of the oxidation of zinc (ZnO) is of more money value than that of the oxidation of carbon, projects have been formed to prepare zinc white by the oxidation of zinc in a cell, utilising the electrical energy as a bye-product, but they have not proved remunerative.

can be reversed by the passage through the cell of a current of electricity from an external source, in a direction the reverse of that taken by the current generated by the cell itself, can be employed as a secondary or storage cell **(accumulator)**. Those cells in which zinc is the attacked metal (unless used in alkaline solutions) are not suitable for employment as secondary cells, because zinc is not readily deposited from a solution containing a mineral acid, so that the chemical change induced by a reversed current will take the form of the decomposition of the water in the cell, and will not go so far as the reduction and regeneration of the zinc. In the case of a compound primary cell, the regeneration of the depolariser is also requisite if the cell is to be used as a secondary cell. This is impracticable with nitric acid and chromic acid cells, but it is possible with a cell using copper sulphate as a depolariser; nevertheless, the Daniell cell is not reversible because the zinc cannot be reduced in the acid solution. The cell consisting of zinc in caustic alkali, and carbon in the same liquid, with CuO as a depolariser, is, however, reversible, inasmuch as zinc can be deposited from an alkaline solution.

The only form of storage battery of commercial importance is that in which lead is used as the attackable metal, and lead peroxide as the depolariser. A cell of this class resolves itself, therefore, into a plate of lead covered with spongy lead, opposed to a second plate of lead covered with lead peroxide, the two plates being immersed in dilute sulphuric acid (specific gravity, 1·18). When this cell is allowed to supply a current by closing the circuit between the electrodes, the spongy lead is oxidised and the lead peroxide is reduced; in each case lead sulphate is the final product. The E.M.F. produced by this chemical change is between 2 and 2·2 volts. Assuming the complete conversion of the surface of both plates into lead sulphate by the discharge of the cell, the calculated E.M.F. is over 3 volts, whilst if the spongy lead plate be alone converted into lead sulphate, an E.M.F. of about 2 volts should result. It is probable that, owing to the insolubility of the sulphate, a coating of the lead or the lead oxide with lead sulphate takes place, and the conversion on both plates is not complete, causing the production of an E.M.F. intermediate between these calculated limits.

Many forms of lead and lead peroxide secondary cells have been devised, but their difference is mechanical rather than chemical. The fundamental type of secondary cells is the Planté, in which the formation of spongy lead and lead peroxide on opposing plates is effected by "forming" the cell by alternately charging it from a dynamo and discharging it; these repeated reversals gradually convert the lead into a spongy state, suitable for rapid oxidation and reduction. The modifications of this fundamental form include cells of the Faure type, in which the spongy lead and lead peroxide are produced by the electrolysis

of lead oxide (generally red lead) applied as a paste to the surface of the lead plates; and modifications of this, in which the active material is held in recesses in a lead grid, or as plugs in a skeleton lead plate, have been devised.

The efficiency of a good secondary cell is about 80 per cent., reckoned on the electrical energy put into it. In spite of this good result, the commercial efficiency is often low, from the cost of repairs, due to the buckling of the plates and separation of the active material from its support. Where accumulators are used as a portable store of electrical energy, their great weight—due to the high specific gravity and atomic weight and comparatively low valency of lead (Pb'')—is seriously detrimental. In spite of this, no metal has hitherto been found effective as a substitute for lead, entirely for chemical reasons.

Another form of storage battery, not yet of practical importance, is that known as **Grove's gas battery.** If a current of electricity be passed into an ordinary voltameter, consisting of two platinum plates immersed in dilute sulphuric acid, and if, after some decomposition of water into H_2 and O has taken place, the platinum electrodes be disconnected from the source of current and coupled to the terminals of a galvanometer, it will be found that a current is generated in the voltameter, and flows in a direction the reverse of that of the charging current. This is due to the fact that each platinum electrode absorbs a portion of the gas (H and O respectively) evolved at its surface; the hydrogen contained in the one platinum plate behaves as the attackable metal of an ordinary cell, whilst the oxygen in the other plate acts as the depolariser of the same cell. The condition and action of the plates of this cell are perfectly analogous to those of the plates of a lead storage battery. The quantity of energy which can be thus stored is limited by the amount of H and O absorbable by the platinum plates, which for plates of ordinary dimensions is small. By the use of a platinum plate coated with platinum black and supplied with hydrogen, opposed to a similar plate supplied with oxygen, both in contact with an electrolyte —*e.g.*, dilute sulphuric acid—a constant current can be maintained, the E.M.F. of which corresponds with that calculated from the heat of combination of the elements of water.

An attempt has been made by Mond to utilise this form of cell for the direct conversion of the chemical energy of hydrogen into electrical energy. The hydrogen for this purpose is prepared from semi-water gas (*q.v.*) by removing the CO and hydrocarbons, which it contains in addition to hydrogen. This is done by passing the gas over pumicestone coated with finely-divided nickel or cobalt at a temperature of 350° to 400° C. = 662° to 752° F. in the case of the former, and 400° to 450° C. = 752° to 842° F. for the latter; the chemical reactions involved are of the form—

$$2CO + Ni_x = Ni_xC + CO_2 \text{ and } C_mH_n + Ni_x = Ni_xC_m + H_n.$$

When the pumice coated with nickel has become clogged with deposited carbon, it can be revivified by the passage of steam according to the equation—

$$Ni_xC + 2H_2O = Ni_x + CO_2 + 2H_2.$$

By such means, gas containing 36 to 40 per cent. of H, and almost completely free from CO and hydrocarbons, can be obtained.

This gas is supplied to a form of gas battery consisting of thin platinum leaf, finely perforated and covered with a film of platinum black, separated by a diaphragm of plaster of Paris (which is saturated with dilute sulphuric acid) from a similarly prepared platinum leaf; the second leaf is supplied with air, which serves as the depolariser. A current corresponding with about 50 per cent. of the calculated chemical energy can be thus obtained. Hourly reversals of the direction of the passage of the air and hydrogen, and therefore of the current, are necessary to prevent the transference of the sulphuric acid from one side of each cell to the other by electric osmosis.* The costly and delicate nature of the apparatus required is against the successful application of this method.

One other instance of the use of a gaseous depolariser is afforded by the chlorine battery, in which gaseous chlorine is applied as a depolariser to a carbon electrode in an ordinary cell.

Except for special purposes, the only method used on a considerable scale for obtaining electrical energy from the chemical energy of fuel, is that in which the fuel is burnt beneath a boiler which supplies steam to an engine, which in turn drives a dynamo. The chemistry of steam-raising will be treated of below. A point of much importance connected with the economy of the dynamo is, however, of chemical interest, and must be mentioned here. It has been found that the efficiency of the iron used for field magnets and armatures of dynamos varies with its magnetic properties; the more rapid and complete its magnetisation and demagnetisation, the better the results obtained. No quantitative relation has yet been arrived at for the influence of the impurities present in commercial iron on its magnetic properties; but, qualitatively speaking, the more nearly pure the iron, the greater the rate of magnetic change and the smaller the amount of residual magnetism which it retains. A full discussion of this matter would be out of place in a work of this scope. The selection of a suitable metal or alloy for the commutator and brushes of the dynamo is obviously also a chemical matter.

NATURAL FORMS OF KINETIC ENERGY.—The foregoing

* This term is applied to the bodily transference of an electrolyte through a porous septum; this is caused by the passage of a current, and takes place in the direction in which the current flows.

examples of sources of energy available for industrial purposes are instances of potential energy capable of becoming kinetic when subjected to suitable conditions. They are examples of a particular kind of energy, namely, chemical energy, and, generally, the first step to their utilisation is their conversion into heat. In less general language they are cases of the energy of fuel which is available for the production of heat by direct burning. In those sources of energy which we are about to consider, the energy is not potential but kinetic—that is, it is actually in course of being expended without the intervention of human agency, and its utilisation can, therefore, be less easily regulated than that of the energy which is locked up in fuel. A concrete case of a form of kinetic energy which exists on the earth and is put to industrial use, is that manifested in a river or a waterfall. It is certain that the energy represented by the flowing water will be expended whether it be turned to commercial account or not, whereas a seam of coal is a form of energy stored in a manner so perfect that it may remain potential for an indefinite period, provided it be not mined and burned. The chief natural forms of kinetic energy are as follows :—

Water Power.—Running water of all kinds may be utilised for obtaining energy in an applicable form. The main conditions of success and economy are that the quantity shall be large, the fall in a given length of the watercourse considerable, and the flow approximately constant. The mean quantity per unit of time cannot usually be artificially increased, but the fall within a given distance can be augmented by the device of forming a dam or weir, and this is commonly done with streams supplying water wheels. The regularity of flow can be aided, though not completely secured, by retaining the water in a reservoir large in proportion to the amount used per day; but, in general, intermittently flowing water is of little industrial value. Where the fall is sudden, as in an actual rapids or waterfalls, it is sometimes impracticable to use the bed of the stream itself for the wheel or turbine, and the water must be diverted and provided with a less precipitous channel. Thus in the scheme now being worked out for the utilisation of the power of Niagara, the water is led into a special channel in which the turbines it is to drive are disposed. Water power is sometimes situated conveniently near mineral deposits which need energy in the form of mechanical power for their working, and it can then be used economically. This is the case in some copper refineries where the electrolytic process is used (see *Copper*). Another instance of the application of water power to the winning of a metal is in the works of the Aluminium Co. at Neuhausen, where the energy requisite to drive the dynamos, the current from which is used in the reduction of aluminium, is derived from a waterfall. Industries that are not conveniently carried out on the spot where water power is avail-

able may, nevertheless, obtain the energy they require therefrom; this is economically effected by converting the water power into electricity, and transmitting high tension currents, which can be used after their conversion into currents at a low pressure, the need for massive copper conductors (in which much capital would be sunk) being thus overcome.

Tides.—Although at first sight only a particular case of water power, tidal energy must be considered separately, as it is derived from a source different from that represented by a stream or waterfall. All the forms of energy that have been dealt with in this chapter—with the possible exception of the chemical energy of petroleum, which may have been derived from the cosmical energy left stored in the earth at the time of its condensation from a nebulous to a fluid condition—are simply forms of solar energy, which has first appeared in some form of life on the surface of the earth, and has been afterwards stored in its crust. This is true, because coal is used almost exclusively for the production of mechanical from chemical energy. Admitting the animal origin of petroleum, which theory has much to recommend it (see *Petroleum*, Vol. II.), the energy present in it would also be referred to the sun. But the energy of the tides is due to the energy of rotation of the earth, sufficing to keep it in motion in spite of the braking action of the mass of water attracted into a huge wave by the moon; every motion of the sea which is tidal and not due to the wind, is of this origin. Consequently, when tidal energy is turned to mechanical account, power is being taken by, as it were, putting a driving belt on the globe, albeit one in which there is a good deal of slip. Hitherto no great success has attended attempts to utilise tidal energy, the range of motion is generally too small, or, if increased by local conditions, such as the bore of a river, too violent and intermittent to allow of steady work. Perhaps the most hopeful method consists in impounding a large quantity of water at high tide, and using it as one would use that from any other reservoir with an available fall. Tidal energy has of course been used for ages in the somewhat crude way of aiding the transport of vessels against a running stream near its mouth.

Wind.—In spite of the variable and intermittent character of the energy that can be obtained from the motion of the air, it is capable of commercial utilisation, and has been so utilised from early times by means of windmills of various design. It is self-evident that if any considerable industry were to be made dependent upon wind power, it would be necessary to collect the energy represented by a large cross-section of the mass of moving air, which we speak of as wind, and to store the energy thus got to provide for the occurrence of a calm. This has been realised on a small scale by the application of windmills to pumping for draining operations and the storage of the

water, or for driving a dynamo and storing electrical energy in accumulators (*v.s.*).

Sun's Heat.—Energy is continually being poured upon the earth from the sun, and is being stored to some slight extent in the liberation of carbon from carbon dioxide by vegetable life,* but is for the most part returned to space by radiation. Numerous attempts have been made to turn it to account by causing it to boil water or other volatile liquid, mechanical work being obtained by the expansion of the vapour of this liquid; but the radiant energy, even when concentrated by a system of mirrors or lenses, is too diffuse and, moreover, too intermittent to be of any tangible use. The only serious application on any considerable scale is in concentrating solutions of salt from sea water, or, in countries destitute of fresh water, distilling sea water for drinking purposes. It has been suggested that the internal store of heat in the earth may be tapped for conversion into mechanical energy.

Value of Natural Forms of Energy.—We have spoken of natural forms of energy, although all energy is natural, in a sense restricted to those cases where kinetic energy occurs in nature. The value of natural kinetic energy may be looked at from two points of view. In the first place, since it is kinetic it will be inevitably degraded into low temperature heat, and it is good economy of the total store available on the earth to turn it to account on its downward path, instead of letting it run wholly to waste. But, in the second place, since its utilisation involves the use of costly plant, it is often commercially economical to disregard it utterly, and rely wholly on the stores of energy in the shape of fuel in one kind or another that would otherwise remain stored for an indefinite time. The circumstances of each case must decide which course is attended by the greater monetary economy; it suffices to say here that the course chosen is not necessarily most economical from an energy point of view. There are many important industries in which the energy required is a small part of the money cost of the whole process, and economy in the energy bill is a secondary matter altogether, and may be sacrificed to convenience or lowness of initial outlay.

The Transmission of Energy.—This chapter would be incomplete without a few words concerning the different methods of transmitting energy that are commonly used. The simplest way of communicating mechanical energy from one moving object to one that is to be moved, is by direct attachment. In the case of a revolving wheel, where the axis of rotation of the wheel to be moved is identical with that already moving, a shaft of the requisite length is an obvious method;

* It has been calculated that 1 square metre of leaf surface will utilise sufficient radiant energy from the sun per day to fabricate 14 grams of dry vegetable substance.

where the axes of rotation are not identical, driving first by frictional contact with the rim, and then by regular rugosities on the rim—*e.g.*, teeth or cogs—suggests itself. A step farther is the transmission of power by belts or ropes, and these are of course freely used. Ropes running at a high speed, and therefore capable of transmitting a good deal of energy without severe pull, are a fairly economical method of distributing power. Water under pressure is another plan that has merits in cases where strong slow motions are especially required, as in most hydraulic machinery, but is less well adapted for any quick running motion, as the friction and inertia of water transmitted through pipes are serious obstacles. Air has fewer disadvantages as a fluid for transmitting power, but energy is lost in compressing it, heat being developed which is dissipated before it reaches the point of consumption. Where any extensive system of transmission of energy by compressed air is in use, it is commonly supplemented by some method of heating the air from an external source before it is used to drive its motor (see p. 63). The best method of transmission through a considerable distance that has hitherto been devised is by the use of electricity. The general plan consists in turning the mechanical energy developed by a steam engine into electricity at comparatively low electrical pressure, converting this by means of a step-up transformer into electricity at high electrical pressure, transmitting through a conductor in the ordinary way, and re-converting it, on the spot where it is to be used, into electricity at low pressure by means of a step-down transformer. Operose as this sounds, it is fairly economical, the least efficient part being the prime mover (that is, the engine and boiler), which has to be employed in any case. The object of using the current at high pressure for the actual transmission, is that the loss by the resistance of the conductor is smaller with a high-pressure than with a low-pressure current, and thus a large conductor of low resistance, which is a very costly piece of plant, because of the comparatively high price of copper, can be dispensed with.

CHAPTER III.

THE CHEMISTRY OF STEAM RAISING.

In modern engineering practice, which is concerned with obtaining mechanical energy from fuel by means of a boiler and engine, much care is displayed in points of design and construction, whilst, on the other hand, but scanty attention is paid to the economical working of the plant, which depends in great measure on purely chemical principles.

WATER.

Next in sequence to the chemical principles concerned in the combustion of the fuel, which are obviously of primary importance and have been dealt with in the preceding chapter, stands the quality of the water used in the boiler; its selection demands careful consideration by the steam-user. Since the general town supply of water for any particular place has been chosen—and filtered or otherwise purified—chiefly in order to fit it for drinking and domestic use, it is often too costly for employment for feeding boilers and other industrial purposes, particularly as the properties which render it suitable for dietetic use are not identical with those characteristic of a good boiler water; recourse is therefore had to a private well, the nature of the water of which must be ascertained by analysis, and then a correction devised for any deleterious action which may be exerted by the water on a boiler, or by the steam in its utilisation, owing to any matter it may carry over in suspension or as a vapour. Most waters which are used for steam raising fall in one of the following classes:—

1. Hard calcareous waters.
2. Soft peaty waters.
3. Saline waters.

This division is not strictly accurate nor exhaustive, as the classes may overlap to some extent, but it serves to define the most commonly occurring waters which are used for steam raising. The source of the supply has a certain relation to the quality of the water, since the strata from which it is derived furnish

characteristic soluble constituents to the water percolating through them. It happens, therefore, that where it is possible in choosing a site for a factory, to pay regard to the surrounding strata, a water of approximately known quality can be procured; thus the chalk formation is sure to yield a hard calcareous water, the same being true of oolitic and other limestone strata; whereas the formations known as the lower greensand and the new red sandstone, generally yield waters which are comparatively soft. Since other circumstances, such as facility of transport, cheapness of fuel, and the like, usually determine the site of a factory, the choice of particular strata whence to obtain water is rarely practicable, and it becomes necessary to deal with whatever variety of water may be locally predominant.

Taking the classes mentioned above *seriatim*, the following description may be given :—

1. **HARD CALCAREOUS WATERS.**—The most characteristic constituent of these waters is calcium carbonate, often associated with magnesium carbonate, both salts being held in solution by carbonic acid. The solvent action of carbonic acid on these carbonates is so marked that it is attributed by some to the formation of bicarbonates (analogous to those of the alkali metals) of the form $CaH_2(CO_3)_2$. It must be noted, however, that the quantity of CO_2 present is almost invariably greater than that which would suffice for the formation of bicarbonate; nevertheless, on the Continent it is customary to indicate that portion of the carbonic acid corresponding with the carbonates which it is instrumental in retaining in solution, by the term "half-bound," to distinguish it from the surplus which is termed "free." Whatever the precise mechanism of the solvent action of carbonic acid on calcium and magnesium carbonates, these salts are invariably precipitated nearly completely when the carbonic acid is expelled by boiling.

In addition to calcium and magnesium carbonates, hard calcareous waters commonly contain calcium sulphate, which is not precipitated on boiling under atmospheric pressure, although when the temperature of the water is considerably above 100° C. = 212° F., as in a boiler, precipitation of anhydrous calcium sulphate, $CaSO_4$, takes place. The crust of calcium sulphate and carbonate deposited at the temperature obtaining in a boiler which is worked at even a moderate pressure, is hard, dense and coherent, and much impedes steam raising, as will be noticed later.

In the absence of calcium sulphate, calcium carbonate generally yields a pulverulent deposit, less objectionable than that given by a water containing both salts. The following are analyses of typical boiler incrustations from hard calcareous waters :—

	I.	II.	III.
	Per cent.	Per cent.	Per cent.
$CaCO_3$, ...	55·65	...	81·10
$CaSO_4$, ...	31·96	97·01	9·86
$Mg(OH)_2$, ...	7·11	0·37	2·58
Water, ...	...	1·75	...
Fe_2O_3 and Al_2O_3, ...	2·10	...	1·48
Silica and insoluble matter, . .	2·46	...	3·54

It will be seen that even at the moderate pressure of 50 lbs. (which is that at which the above incrustations were formed) calcium sulphate is freely precipitated. The occurrence of magnesia in the form of hydroxide in the incrustation, will be discussed in a later paragraph.

It is customary to speak of water containing salts of calcium and magnesium as "hard," the term being especially used as indicating their soap-consuming power when such waters are employed for washing—a hard water being one which consumes much soap before a lather can be produced in it. The first action of soap on a hard water is to precipitate calcium and magnesium salts of the fatty acids of the soap. The curdy precipitate thus formed is useless as a detergent, and it is not until the soap itself passes into solution that a lather is produced, this lathering being a characteristic property of a soap solution. A distinction is usually drawn between **temporary hardness** and **permanent hardness.** The former is caused by the presence of calcium and magnesium carbonates, which are precipitated in great measure when the water is boiled, and on this account may be considered as temporary hardening agents. The latter is due to the other salts of calcium and magnesium which are not precipitated when the water is boiled—*e.g.*, the sulphates, chlorides, and nitrates; with regard to calcium sulphate it must be remembered that it is precipitated when the water is heated to a temperature above its normal boiling point—that is, under pressure in a boiler. It follows from this that the mere statement of either temporary or permanent hardness, or of both, is no guide to the character or amount of the boiler scale which will be formed, and a complete mineral analysis of the water is requisite, even this being only a guide towards the formation of an opinion by the chemist as to the behaviour of the water under conditions comparable with those obtaining in practice.

In general, hard calcareous water, producing much scale, is not liable to cause, in addition, corrosion of the boiler, both on account of its inherent qualities (see *Saline waters*), and because of the protective effect of the scale deposited.

The following analyses give the quantities of salts commonly found in hard calcareous waters :—

	Grains per Gallon.			
$CaCO_3$, . .	15·23	12·86	23·72	19·55
$CaSO_4$, . .	12·04	...	7·31	16·08
$MgCl_2$, . .	...	...	6·29	28·71
Na_2SO_4, . .	6·97	12·67	...	...
NaCl, . .	4·70	25·39	29·82	20·25

2. **SOFT WATERS** (containing little mineral matter).—Rain water collected artificially is a typical soft water, containing but a trifling amount of mineral matter in solution. Streams fed with rain water and running through districts containing little vegetation, yield a water standing near to rain water in respect of its content of mineral matter. The majority of soft waters, however, on account of the absence of calcareous matter, dissolve peaty matter from the vegetation which they encounter on their course. These peaty substances consist largely of vegetable acids, the calcium salts of which are insoluble in water, so that they are not dissolved by hard waters. Their feebly acid character renders peaty waters liable to attack boiler plates, and the slimy nature of the salts which are produced by such attack causes them to form an objectionable incrustation (*v.i.*).

As peaty waters, in common with all natural waters, contain dissolved oxygen, their action on metallic pipes and plates is enhanced by the fact that any oxide formed by the action of the dissolved oxygen is basic in character and will combine with the peaty acids, rendering the corrosion of the metal more serious. The action of the acids in this respect is similar to that of CO_2 in the attack of iron by atmospheric oxygen (see Chapter I., p. 39). Such waters are also peculiarly liable to act on lead.

The following are analyses of soft peaty waters :—

	I. Water of the Wye (Phillips). Grains per gal.	II. Moorland Water. Grains per gal.
NaCl, ...	1·04	1·07
$CaCl_2$, ...	0·06	...
$Ca(NO_3)_2$, ...	0·09	0·41
$CaSO_4$, ...	1·12	...
$CaCO_3$, ...	2·88	0·77
$MgCO_3$, ...	0·95	...
SiO_2, . . } Fe_2O_3 and Al_2O_3, } . . .	0·26	...
Organic matter, . . .	0·27	...
Na_2SO_4, ...	...	0·71

3. **SALINE WATERS.**—An extreme example of a saline water used for boiler purposes is sea water. The following analysis of water from the Irish sea (*Thorpe*) represents the average composition of sea water; although considerable varia-

tions in concentration occur locally, the ratio of the salts to each other is nearly constant:—

	Parts per 1,000.*
$NaCl$,	26·44
KCl,	0·75
$MgCl_2$,	3·15
$MgBr_2$,	0·07
$MgSO_4$,	2·07
$CaSO_4$,	1·33
$CaCO_3$,	0·05
Iodine,	Trace

When sea water is used in a boiler a concentration is soon reached at which the soluble salts begin to separate. This point is indicated by the specific gravity of the concentrated water, and for its determination it is customary to ascertain the specific gravity of the liquid in the boiler from time to time by means of an hydrometer called a **salinometer**. When this concentration is attained the water must be blown out. When very saline waters are used for steam raising the adoption of condensing engines is advantageous, as it allows of the return of the major part of the water which has passed through the cylinders as steam, to the boiler, and thus concentration to the crystallising point is greatly retarded.

Brackish water drawn from rivers (near their mouths) and from estuaries may be regarded as diluted sea water. A great objection to its use arises from its variable character, as its composition depends on the proportion of sea water locally and temporarily present. Since sea water contains calcium sulphate, which salt is deposited in a boiler (*v.i.*), it follows that, even when used to a concentration short of that at which the deposition of ordinary soluble salts begins, sea water will yield an incrustation, the nature of which is shown by the following analysis (*Lewes*):—

	Per cent.
$CaCO_3$,	0·97
$CaSO_4$,	85·53
$Mg(OH)_2$,	3·39
$NaCl$,	2·79
SiO_2,	1·10
Fe_2O_3 and Al_2O_3,	0·32
Organic matter,	Trace
Moisture,	5·90
	100·00

The presence of $Mg(OH)_2$ in the boiler deposit from sea water is caused by the decomposition of magnesium chloride at the high temperature obtaining in a boiler (the dissociation of this salt

* Thus stated, instead of in the more usual nomenclature (grains per gallon), on account of the great concentration of sea water as compared with ordinary saline waters.

being readily effected on evaporation), and also by the decomposition of magnesium carbonate formed by the interaction of calcium carbonate with the soluble magnesium salts present in excess. Such portion of the magnesium hydroxide as results from the decomposition of magnesium chloride is a measure of the corrosive effect of this last-named salt on the boiler plates, for it will be obvious that the deposition of magnesium hydroxide involves the liberation of an equivalent quantity of HCl if its source be simply magnesium chloride without the intervention of calcium carbonate in the manner spoken of above. It is known that magnesium chloride, when heated in presence of water, readily decomposes into magnesium hydroxide or an oxychloride, and hydrochloric acid; in aqueous solution this does not take place until considerable concentration has occurred, but it is probable that in a boiler dissociation is promoted by the higher temperature attained; local over-heating of the salt, already separated from its solution on parts of the boiler above the water line, may also take place. These two actions suffice to produce the corrosive effects observed, which, owing to the volatility of HCl, may extend to all parts traversed by the steam—*e.g.*, steam pipes and cylinders. Local action caused by these circumstances may occur in spite of the feed water being alkaline from the presence of calcium carbonate, as the incrustation formed by this salt will only afford protection below the water line.

A marine boiler incrustation will contain calcium sulphate as the chief constituent, and magnesium hydroxide as the main secondary constituent; the following analysis (*Lewes*) will serve as an example in addition to that on p. 102 :—

	Per cent.
$CaSO_4$,	84·27
$Mg(OH)_2$,	7·04
Sand,	1·94
Fe_2O_3 and Al_2O_3,	1·10
Water, &c.,	5·65
	100·00

Many waters derived from mines contain large quantities of saline constituents, especially sulphates, often derived from the oxidation of pyrites and other sulphides. The following analysis (*Allen*) is an example of a mine-water rich in sulphates :—

	Grs. per gallon.
$CaCO_3$,	10·8
$CaSO_4$,	16·0
$MgSO_4$,	20·4
Na_2SO_4,	73·6
NaCl,	70·4

When calcium carbonate is absent, free sulphuric acid often exists in waters of this class, leading to serious corrosion of pumping machinery.

The life of the boiler depends on several factors, of which the character of the water, considered above, is one of the chief. Hard calcareous waters form scale in the manner already described, and in this respect are injurious to the economy of steam raising, partly by damaging the boiler itself, and partly by wasting the fuel required. The latter is a serious evil, for the incrustation is a badly conducting material, and, by impeding the transmission of heat from the furnace to the water, diminishes the output of steam from the boiler, if the furnace is fired normally—that is, at a rate approximate to the absorption of heat by the "heating surface" exposed by the boiler. To compensate for this diminished output of steam, the natural action of the stoker (often necessary when the full output of the boiler is required) is to increase the rate of firing, with the result that the extra quantity of heat generated in the furnace is only imperfectly absorbed by the boiler, and goes to waste in the flue gases. It has been found that an incrustation of $\frac{1}{6}$ inch thick causes the use of about 16 per cent. more fuel than would be necessary with clean plates, whilst one which is $\frac{1}{4}$ inch thick involves a waste of as much as 50 per cent., and one of $\frac{1}{2}$ inch a waste of 150 per cent. The damage to the boiler itself is due to two causes—(1) the deterioration of the plates by overheating, and (2) the mechanical damage involved in removing the incrustation. A coated boiler plate is necessarily hotter than when clean, as the water is kept from free contact with it. Thus, whereas a clean iron vessel containing water boiling under atmospheric pressure has a temperature not more than 10° C. above the boiling point of water, one with an incrustation so thin as $\frac{1}{16}$ inch may have a temperature more than 100° C. higher. The mechanical properties of the metal composing the boiler plates are considerably modified even by the temperatures proper to modern pressures—*e.g.*, 150 to 200 lbs. of steam, corresponding with 370° to 400° F. = 188° to 204° C.—and are still more affected when there is extra heating on account of the presence of an incrustation.

In the case of boilers of the water tube or of the locomotive class, a further difficulty arises from the incrustation—namely, the blocking of the tubes or of the spaces between them with scale, and consequent hindrance of circulation of the water. In aggravated instances actual stoppage of a water tube may occur, involving its speedy destruction by its exposure to the fire without being simultaneously cooled with contact with the water.

The evils of heavy incrustation are sufficiently well recognised to lead to the practice of periodically chipping the scale from the boiler plates, a troublesome operation, liable to cause injury to the boiler, and best avoided by removing the cause of incrustation. Although a water yielding a heavy or even a moderate scale is thoroughly objectionable, one giving a slight film of calcium

carbonate or sulphate is not wholly harmful, on account of the protection which it affords against corrosion from the several sources now to be mentioned.

When saline waters are used which contain calcareous salts, the incrustation formed and the damage caused will be similar to those arising from calcareous waters proper. As magnesium chloride is frequently present in saline waters, a corrosive effect on the boiler also occurs from the cause described above; such corrosion will not take place below the water line if a protective incrustation be formed; but serious weakening of the boiler will result from the attack of the plates above the water line, since the corrosion is not uniform, but local, for a reason stated below. Of course mine-waters in which free acid is present will cause serious corrosion, and must be treated before use, particularly if containing the salts of metals reducible partially or entirely by iron—*e.g.*, Cu, and Fe in the ferric state. With copper salts the copper is first reduced at the expense of the iron of the boiler, and then forms with the plate an iron-copper couple, of which the iron is the attackable metal. With regard to ferric salts, direct reduction to ferrous salts, necessitating the solution of an equivalent of iron, takes place, and if oxygen be present the ferrous salts formed by this reduction act as carriers between the oxygen and the iron of the boiler.

Soft waters which cause no incrustation, save that due to peaty matter—concerning the action of which but little authentic information has been obtained—and having but trifling saline constituents, are nevertheless liable to cause damage by corrosion. As all natural waters that have been freely exposed to the air are nearly saturated with oxygen, the quantity present being, at 15° C. = 59° F., 10 mgms. per litre,* all would be liable to cause oxidation of iron in a boiler, were it not that those which are calcareous form a protective incrustation which diminishes the damage done. In the case of waters not yielding an incrustation—*e.g.*, soft peaty waters—the influence of dissolved oxygen on the metal of the boiler is more marked, its action being identical with that of ordinary rusting (*q.v.*)—(*cf.* p. 101).

* This limit of saturation is, of course, influenced by the partial pressure of O in air. A higher figure is given by pure oxygen. The following table shows the solubility in c.c. per litre of water of the three chief gases normally present in water at various temperatures and at a pressure of 760 mm. exerted by each gas:—

	0° C.=32° F.	10° C.=50° F.	20° C.=68° F.
O, . . .	42	33	28
N, . . .	20	16	14
CO_2, . .	1,797	1,185	901

Corrosion chiefly occurs at the water line, the reason apparently being that the oxygen is rapidly expelled from the water on heating and then attacks the iron where it is wet but not covered with water; a second cause, having a like effect, is the tendency of the bubbles as they are expelled during the heating of the water, to cling to the sides, especially at the surface. It will be remembered that the gases dissolved in water are relatively richer in oxygen than is the air from which they have been derived, the ratio of O to N being approximately 1 : 2; this circumstance enhances the corrosive action.

In view of recent experiments showing that steel wire which has been exposed to boiling water (at 760 mm.) has a lower tensile strength than that which it previously possessed (a diminution of about 20 per cent. in 84 days), it appears probable that, in the absence of an incrustation, a similar weakening of the boiler plates may occur. The cause of this alteration is probably the decomposition of a portion of the water at the temperature of the boiler by the iron, and the absorption of the hydrogen resulting from that decomposition, for it is known that iron which has absorbed hydrogen is more brittle than the metal in its ordinary state (see Footnote, p. 28).

A form of incrustation which is peculiarly harmful both to the economical working and to the life of a boiler, is that formed when oily matter obtains access to the feed water, and thence passes into the boiler. When animal or vegetable oils are used as lubricants in the cylinders of the steam engine (see *Lubricants*), hydrolysis of the oils may occur by the action of the high-pressure steam, aided by the presence of metallic oxides from the material of the cylinder, and fatty acids may be volatilised with the exhaust steam into the condenser of the engine, and thus pass with the feed water to the boiler. Even when mineral oils are used as lubricants and no hydrolysis can occur, a portion of the mineral oil may be distilled over with the steam, in spite of the temperature of the cylinder being below that at which distillation occurs when the mineral oil is heated *per se*, and may similarly find its way into the boiler. In the case of fatty oils, the acids derived from them form lime soaps with the lime in calcareous boiler water, and are deposited in this form as an adherent oily incrustation, very badly conducting in character. Mineral oil, on the other hand, will attach itself mechanically to calcium carbonate and sulphate during their deposition from the water, forming with them oily globules which eventually coat the plate with a non-conducting incrustation. Thus, in either case, the plates are more thoroughly protected from contact with the water, by reason of the oily character of the incrustation, than is the case when the incrustation is purely calcareous. Overheating and collapse of plates thus coated consequently take place. A scale of this

kind was found by Lewes to have the following composition:—

	Per cent.
$CaSO_4$,	59·11
$CaCO_3$,	6·07
$Mg(OH)_2$,	11·29
Fe_2O_3, Al_2O_3, SiO_2,	2·85
Organic matter and oil,	19·54
Moisture,	1·14
	100·00

It remains to consider the nature and mechanism of the corrosion to which a boiler may be subjected, both internally and externally. The general process of corrosion is identical with that described under the rusting of iron (see p. 39); certain points, however, need separate mention. Thus, local corrosion or "pitting" is liable to occur. By this term is meant the formation of small hollows or depressions in the boiler plates indicating rapid local attack, which may lead to the necessity for renewing a much larger area than that which is actually damaged. The cause of this local action is to be found either in the composition of the attacked plate, or in the nature of the mode of attack, or in both. A plate of ingot-iron such as is used for boiler making, may have its impurities, notably manganese and sulphur, irregularly distributed throughout its mass. Spots rich in these impurities will suffer corrosion more rapidly than other parts, possibly because of the formation of a galvanic couple between adjacent portions of the plate which are of different composition. Similarly, the impurities, including the slag, which are characteristic of puddled iron (still sometimes used for boiler making), are not uniformly diffused through the metal, and the places richest in these impurities will be more readily corroded, the mechanical looseness of structure due to the presence of the slag, often aiding this effect.

Particles of brass and copper finding their way into a boiler, sometimes act as centres of corrosion by setting up galvanic action in which the iron is the metal attacked. This is especially the case when most of the surrounding iron is protected by incrustation, the corrosive action being thus localised, consequent on the increase in current density arising from restriction of the surface of the larger electrode.

Local corrosion of iron sometimes arises from the trapping of air bubbles in slight hollows already existing, and the oxidation and deepening of these spots by successive portions of entrapped air. Pitting, however, from localised causes other than those arising from the nature of the metal, is not common in boilers, because any liquid or gaseous corrosive substance introduced into the boiler tends to be diffused over all the exposed surface

by the agitation and circulation of the water and atmosphere in the boiler.

The external corrosion of a boiler shell differs in no essential respect from the corrosion of other structural iron, which has been already dealt with in the first chapter of this section.

The same protective effect that is obtained by "galvanising" iron, is sometimes secured for a boiler by hanging zinc plates or spheres in the water, with the object of diverting attack thereto and saving the boiler plates; the action is a galvanic one in which the zinc is the attacked plate.

SOFTENING AND PURIFICATION OF BOILER WATER.—After a water intended for use in a boiler has been analysed and its mineral constituents determined, it is possible to pronounce whether it can be used in its natural state, and, if not, what treatment it must first undergo. In considering water purification it is convenient to divide the impurities which need removal into two classes—namely, those which are precipitated on boiling the water under atmospheric pressure, and those which are not deposited under such conditions. In the first class calcium carbonate is the commonest impurity; the behaviour of magnesium carbonate is similar but not identical, as its deposition from boiling water is less complete than that of calcium carbonate. A saturated solution of calcium carbonate in water saturated with CO_2 at 10° C. = 50° F. and 760 mm., contains 61·6 grains per gallon of this salt, and one of magnesium carbonate under like circumstances contains 2,030 grains per gall. On boiling such solutions at atmospheric pressure, the bulk of each salt is precipitated, the amount left in solution being about 2·5 grains per gallon for calcium carbonate, and 7 grains per gallon for magnesium carbonate. In actual boiler waters such a condition of saturation does not occur, but the quantities of $CaCO_3$ and $MgCO_3$ left in solution when the water is boiled at atmospheric pressure, are approximately those just given, although some allowance must be made for the solvent influence of other salts simultaneously present. It is evident from this that the bulk of these carbonates can be removed by boiling the water previous to its admission to the boiler; this is practised when feed water is heated by waste steam, a deposit being then produced in the heater instead of in the boiler.*

The same action occurs in reservoirs used to store water at a high temperature and pressure outside the boiler—in order to meet emergency demands, as in the case of boilers at electric lighting stations—with the addition that $CaSO_4$ is also thrown down. In many cases, as in non-condensing engines utilising the exhaust steam for producing a furnace draught, pre-heating

* Mere heating under atmospheric pressure only frees the water from $MgCO_3$ and $CaCO_3$, and leaves untouched the still more objectionable scale-forming constituent, $CaSO_4$ (*v.i.*).

the feed water is impracticable, and the removal of $CaCO_3$ and $MgCO_3$ must be otherwise effected.

The process usually adopted consists in adding lime to the water to be softened, in amount just sufficient to combine with that quantity of CO_2 which is concerned in holding the $CaCO_3$ and $MgCO_3$ in solution, whether it exist as bicarbonate or in the free state. If the CO_2 were present in the proportion indicated by the formula $CaCO_3,H_2CO_3$ (the calcium bicarbonate sometimes assumed to exist, see p. 99), the quantity of lime requisite would be equivalent to the lime and magnesia present as carbonates in the water. Such relation between the carbonates and the CO_2 is not found in natural waters, there being always an excess of CO_2, necessitating a larger amount of lime to effect the softening than that which corresponds with the $CaCO_3$ and $MgCO_3$ present. The function of the lime is to combine with the CO_2 other than that present as $CaCO_3$ and $MgCO_3$, to form $CaCO_3$; this is precipitated, and, simultaneously, pre-existing $CaCO_3$ and $MgCO_3$ are also precipitated.

In practice, where space permits, the lime is best added in the form of lime water, made by stirring excess of lime with water until saturation is effected, and allowing the undissolved lime to settle; the clear liquid contains about 100 grains of CaO per gallon, and is more reliable in its action than milk of lime, inasmuch as its composition is always known, whereas milk of lime may vary largely in content of CaO. Where space is limited, and a separate tank for the preparation of lime water cannot be used, a weighed quantity of lime, sufficient for treating a known volume of water, is stirred into a cream with a little water, and added to the contents of the tank in which the softening is to be carried out. To ascertain whether an excess of lime has accidentally been added (such excess being objectionable, as it causes formation of incrustation in a boiler), some test which will show whether calcium hydroxide is present in solution, must be applied to a small filtered portion of the water. Tests commonly in use for this purpose consist in the precipitation of silver oxide from the nitrate, of mercuric oxide from mercuric chloride, or in observing the reaction with phenolphthalein. With waters containing magnesium salts, such as the chloride, the first effect of lime in excess of that necessary to combine with the CO_2 is to decompose these magnesium salts, and a portion of the resulting magnesium hydroxide remains in solution until the water is heated, when it is deposited, frequently on the injectors and other feeding apparatus of the boiler. This drawback is met by Archbutt by passing furnace gases into the treated water, the CO_2 thus introduced serving to carbonate any excess of lime or any magnesia that may be present, with at most, the effect of producing a slight scale in the boiler. The proper amount of lime, either in solution or as a cream, having been added, and

thoroughly mixed with the water; separation of the precipitate can be effected either by subsidence or filtration. The former is the simpler, the latter the more rapid method, and choice between them depends on local circumstances. This process of lime treatment was originated by Clark, improvements in filtration having been added by Porter, whence the term "Porter-Clark process," as applied to precipitation by lime and filtration through filter presses. It will be understood that this process is only adapted for removing that portion of the incrustation-forming constituents which is precipitated when the water is boiled under atmospheric pressure, and that it is without action on others—*e.g.*, $CaSO_4$; moreover, a certain amount of $CaCO_3$ and $MgCO_3$, corresponding with the solubility of these substances, remains in solution. With these limitations the process is efficacious in dealing with many hard calcareous waters.

When ferrous carbonate is present in a water, this will also be precipitated on treatment with lime; mere aeration will also suffice to remove it, since it oxidises, yielding ferric hydroxide or basic carbonate, which is insoluble in water. The precipitate should be separated by subsidence, as it causes the oxidation of the cloth of the filter press, acting as a carrier of oxygen from the air to the fibre.

Since the water in the boiler is used at a temperature above 100° C., often attaining, in high-pressure boilers, 150° to 200° C. = 302° to 392° F., it is not sufficient to treat the water so as to remove merely those substances which are precipitated on boiling under atmospheric pressure, particularly as these substances are not the worst offenders in the formation of scale. Calcium sulphate is the most objectionable constituent of a boiler water of the hard calcareous class, since it forms with the $CaCO_3$, which is generally simultaneously present, a particularly dense and adherent scale, the reason for the deposition of which has been already dealt with at p. 99. The usual method of treating waters containing $CaSO_4$ consists in the addition of sodium carbonate, which forms calcium carbonate and sodium sulphate by double decomposition with the $CaSO_4$. When the water also contains $CaCO_3$ and $MgCO_3$, it may be first freed therefrom by addition of lime, and then further purified from $CaSO_4$ by Na_2CO_3. The softening agents can be added together, when they become, in effect, a mixture of caustic soda and calcium carbonate (when equivalent quantities are used), or these substances together with an excess of either original reagent (when the quantities do not happen to be equivalent). Caustic soda alone can be used when the amount of CO_2 to be saturated is precisely equivalent to the quantity of calcium sulphate to be precipitated by the resulting sodium carbonate. When this relation does not obtain, the caustic soda must be supplemented by lime, should the CO_2 be present in greater

amount than that equivalent to the $CaSO_4$ contained in the water, but by sodium carbonate should the amount of CO_2 be smaller than this equivalent. The following equations will make these relations clear:—

(1) $CO_2 + 2NaOH = Na_2CO_3 + H_2O$.
(2) $Na_2CO_3 + CaSO_4 = Na_2SO_4 + CaCO_3$.

If the sodium carbonate produced according to the first equation be more than sufficient to precipitate the whole of the $CaSO_4$ in accordance with the second equation, a portion will remain in solution, and both constitute a waste and be injurious from a steam-raising point of view. On the other hand, if the CO_2 in the first equation be insufficient to produce enough sodium carbonate for the realisation of the second equation, the whole of the $CaSO_4$ will not be precipitated, and the water will still yield an incrustation. Save in so far as it allows of the use of a more compact form of softening agent, the use of caustic soda is less to be commended than that of lime and sodium carbonate in the correct proportions, except where filter presses are to be used, and the total precipitate to be handled must be kept at a minimum.

An attempt has been made to substitute magnesia for caustic soda as a precipitating agent, the method consisting in filtering the water through sawdust mixed with MgO. The first effect is to precipitate $CaCO_3$ and $MgCO_3$ by saturation of the CO_2 which keeps them in solution, the resulting magnesium carbonate from both sources then reacting with the $CaSO_4$, forming $MgSO_4$ and $CaCO_3$; a certain amount of $MgCO_3$ remains in solution, but its deposition on the boiler is not greatly objectionable, as the sludge formed is loose and non-adherent. The presence of magnesium salts in solution, however, makes the formation of magnesium chloride and its subsequent decomposition in the boiler probable, and is, so far, undesirable. Other methods—chiefly of chemical rather than of technical interest, on account of the cost of the materials—for treating boiler waters containing $CaSO_4$, are those involving the use of barium chloride and of sodium fluoride; the former decomposes the $CaSO_4$ by double decomposition, yielding calcium chloride and barium sulphate, which, however, settles slowly; the latter gives calcium fluoride, a somewhat voluminous precipitate, sodium sulphate remaining in solution.

Attempts have been made to deposit all the incrusting substances which are present in the feed water, in the boiler itself, not allowing the deposit to be distributed generally over the surface of the boiler, but confining the deposition to spots accessible for cleaning out. Of this type is an apparatus consisting of a delivery tube for the feed water, passing through the water space of the boiler, and having its exit end above the water level. $CaCO_3$, $CaSO_4$, &c., are deposited in this feed pipe before the water debouches into the boiler itself, and can be mechanically

removed. The success of devices of this class chiefly depends on allowing the feed water to travel slowly to its exit, so as to allow time for complete deposition. It must be understood that the trouble of incrustation is not removed, but transferred from the boiler to the feeding apparatus.

Various plans have been suggested for overcoming the sluggish subsidence of the precipitate obtained when certain waters are softened, notably those drawn from a river instead of a well, and containing organic and clayey matter in suspension. A simple and efficacious plan consists in leaving the sludge from the first purification in the precipitating tanks in which the next batch of water is to be treated, and agitating this sludge with the water during treatment. The coarse preformed precipitate induces the deposition of the freshly-formed, finely-divided precipitate. A small quantity of alum, aluminium sulphate, or ferrous sulphate is sometimes added together with the lime; the flocculent oxide of aluminium or iron thus precipitated entangles the suspended matter and hastens clarification.

It must not be supposed that a water when free from constituents capable of forming an incrustation is necessarily suitable for boiler use. If hard with calcium sulphate, the removal of this substance by means of sodium carbonate leaves in solution an equivalent of sodium sulphate, which, if present in large quantity, is found to cause "priming" in the boiler. (By the term **priming** is meant such tumultuous ebullition as causes the projection of finely-divided water, as spray, into the steam space, whence it travels to the cylinder, causing bad economy in the working of the engine.) Excess of sodium carbonate added to the water has the same effect, and natural waters containing sodium carbonate (which are not uncommon) of course act similarly. Such waters may even have to be treated with calcium chloride to decompose the sodium carbonate and leave the comparatively harmless sodium chloride.

Boiler Compositions.—To avoid the cost of the plant necessary for removing the scale-forming constituents in a feed water, it is customary, especially on the part of small power users, to add some composition to the water in the boiler with a view of preventing the deposition of a coherent incrustation. Many proprietary preparations are sold for this purpose, of which it is sufficient to say that none should be used without a knowledge both of its composition and of that of the water to be treated, and that all are sold at prices bearing but a remote relation to their intrinsic values.

Caustic soda or soda ash (Na_2CO_3) forms the basis of a very large number of these **anti-incrustators**; these are effective when used in the proportion demanded by the particular water to be treated, but may cause priming if added in excess. They owe their virtue to the fact that they decompose calcium car-

bonate and sulphate, with the result that the deposition of calcium sulphate is avoided and the incrustation is comparatively loose. The prevention of a dense adherent scale being the object of the use of these preparations, any salt capable of forming a non-cohering precipitate with the calcium sulphate in a hard water may be employed, provided it has no objectionable action of its own; for example, sodium phosphate and barium chloride are constituents occasionally adopted. The decomposition of calcium carbonate in the boiler is sometimes achieved by preparations containing ammonium chloride, which forms calcium chloride and ammonium carbonate; the latter substance is deleterious, since it is volatile and exercises a corrosive action on copper and its alloys forming parts or fittings of the boiler.

Other anti-incrustators which have for their object the formation of a loose sludge in place of a coherent scale, are efficient to some extent in that they contain amorphous organic rubbish—peat, sawdust, &c.—which hinders the mutual adherence of the scale-forming constituents of a boiler water. A similar result is arrived at by employing tannin and other vegetable extractive matters; in this case the action is aided by the formation of the lime salts of slightly acid substances of the character of tannic acid. An objection to fatty substances, which have also been exploited, has been already stated under the head of oily incrustations (p. 106). Anti-incrustators have their value under certain conditions of limited space or smallness of plant, but if adopted they should be bought under their own names and at their own market prices, instead of at fancy rates under proprietary titles.

CHAPTER IV.

THE CHEMISTRY OF LUBRICANTS AND LUBRICATION.

THE function of a lubricant being to keep the surfaces on which it is smeared from coming into contact with each other, and at the same time to allow of their motion relative to each other to take place with as little impediment as possible, it is obvious that a special class of bodies must be used for these purposes, having particles which slide easily over each other, while having sufficient cohesion to prevent the ready rupture of a film composed of them.

A further result of this conception of the functions of a lubricant is the realisation of the fact that the speed with which the surfaces move over each other, and the pressure tending to force them together, must be considered in choosing any individual from the class fitted for a given kind of work. The logical outcome of this is that every different kind of bearing needs a different lubricant to enable it to run with the least friction. In practice it suffices to use a different kind of lubricant for each different class of bearing, even when the members of the class are not identical. The disadvantage of using a lubricant not the absolutely best for the bearing, is more than compensated for by the advantage of having comparatively few kinds of lubricants to provide and distribute.

Oils may be regarded as typical lubricants. Fatty oils, that is to say, oils consisting of the glyceryl salts of acids of the fatty and similar series, have been almost exclusively used until comparatively modern times. Since the rise of the petroleum industry it has been found that certain of the fractions obtained in distilling crude petroleum, which are intermediate between the light burning oils and the heavy pitchy residue, are excellent lubricants, possessing important properties which give them, in some respects, the preference over fatty oils; they are, accordingly, largely prepared and used. Of solid lubricants there is a considerable variety, the individual members of which are chiefly used where exceptionally heavy loads are to be carried, or where, as in outdoor use, a cheap lubricant that will not drain or be washed away, is wanted. Such are axle grease, cart grease, black lead, tallow, and soapstone compositions.

FATTY OILS.—For a fatty oil to be of use as a lubricant it is essential that it should be non-drying (see *Oils*, Vol. II.). It is also desirable that it should not readily become rancid, as

during the change understood by the phrase "becoming rancid," free fatty acids are produced, which have a corrosive action on metallic surfaces with which they are in contact. The soaps of the heavy metals thus formed are pasty substances of too sticky a nature to be serviceable as lubricants. Oils which fulfil these conditions are sperm oil, neatsfoot oil, lard oil, castor oil, and, in smaller degree, olive oil, tallow, and rape oil. The first four are specially free from tendency either to dry or to become rancid, and are, therefore, the best examples of their class. Choice between them depends on their viscosity or "body," sperm oil being a light oil of low viscosity, which, however, it retains as the temperature rises, whilst neatsfoot oil and lard oil are of greater viscosity, but diminish in body with rise of temperature to a greater extent than does sperm oil. Castor oil is distinguished by its great viscosity, on which account it is used for lubricating heavily loaded journals. With regard to the remaining three, olive oil is a good lubricant if originally free from fatty acid, and not allowed to become rancid in use; rape oil is also useful on account of its high viscosity, the advantage of which compensates in great measure for the drawback arising from its tendency to gum. Tallow is esteemed for heavy loads and high temperatures, and is, therefore, used for cylinder lubrication, but is apt to be decomposed by high pressure steam, and consequently to yield fatty acids and their salts of iron, copper, by action upon metals with which it is in contact.

In stating the viscosity of an oil, it is usual to adopt the viscosity of rape oil at 60° F. as a standard and to call it 100. The oils described above have at 60° F. = 15·5° C. viscosities which, referred to this standard, are represented by the following figures:—

Sperm oil,	32
Neatsfoot oil,	87
Lard oil,	88
Castor oil,	1,100
Olive oil,	72
Rape oil,	100

The difference in drop of viscosity in oils of this class is shown in the following table:—

Oil.	Viscosity at		
	15·5° C. = 60° F.	50° C. = 122° F.	100° C. = 212° F.
Sperm oil,	32	19	15
Olive ,,	72	24	16
Rape ,,	100	30	17
Castor ,,	1,100	157	27

These figures indicate the class of work for which each of the foregoing oils is most suitable, it being a general rule that for quick-running bearings, carrying low pressures, an oil of low viscosity is best fitted, whilst for heavy pressures an oil of higher viscosity is required. Furthermore, where a bearing is liable to rise in temperature during use, it is desirable that the oil employed for lubricating it should change as little as possible in viscosity with rise of temperature. In selecting an oil its viscosity must be considered as regards the temperature which is likely to prevail during the running of the bearing; at temperatures above and below this the oil will not be working to the best advantage, but such imperfection is of little practical moment, if the viscosity be adapted for the mean temperature of the bearing.

The classes of bearings which may be lubricated economically by the oils spoken of above, are indicated in the following synopsis:—

Sperm oil, .	. Quick running spindles lightly loaded.
Neatsfoot oil,	. Bearings exposed to low temperatures and mechanism in which risk of corrosion is specially to be avoided (*v.i.*)—*e.g.*, *clocks*.
Lard oil, .	. Shafting, engine, and machinery bearings.
Castor oil, .	. Bearings working at heavy pressures and high speed.
Olive oil, .	. Moderate pressure and high speed.
Rape oil, .	. Engine bearings and cylinder lubrication.*
Tallow, .	. Cylinder lubrication.*

All fatty oils in their condition as expressed or rendered, contain free fatty acid, varying in amount from about 1 per cent. in the case of good sperm oil, to 10 per cent. for common olive oil (calculated as oleic acid). It is a sound general principle that lubricating oils should contain the least possible quantity of free fatty acid; 4 per cent. (calculated as oleic acid) is the maximum permissible. Oils that are refined by treatment with sulphuric acid—*e.g.*, rape oil—are liable to contain traces of this acid, either free or in the form of a sulphonic acid. This impurity is highly objectionable for lubrication.

It must be remembered that all fatty oils tend to develop free fatty acids on keeping and in use (see *Oils*, Vol. II.), and that on this account a sample originally nearly free from free fatty acid may become acid to an objectionable extent during use. Olive oil is the worst, in this respect, of those mentioned above. As the temperature rises, the tendency for the development of free fatty acid increases, and when the oil is also in contact with high-pressure steam, hydrolysis occurs freely and much fatty acid is liberated.

The general character of the fatty lubricating oils is given in the section on fats and oils.

* No fatty oil is really suitable for cylinder lubrication.

MINERAL OILS.—These are all higher fractions of petroleum and shale oil, and are produced in many different grades, ranging from a light oil as thin as sperm to a semi-solid mass resembling axle grease in consistency. The exact grade to be used in any given case is determined by consideration of the load to be carried and the speed of the journal; the higher the speed and the lighter the load, the thinner the oil that will give the best results. The following table gives the viscosity of oils at different temperatures suitable for distinct classes of bearings, the viscosity of rape oil at 60° F. = 15·5° C., being taken as 100:—

	60° F. = 15·5° C.	140° F. = 60° C.	180° F. = 82° C.	220° F. = 104° C.
Cylinder, . . .	Semi-solid	30	17	12
Medium machinery, .	100	19	13	10
Spindle, . . .	53	9	5	3

When once the best oil has been decided upon, future supplies of satisfactory quality can be obtained by comparing the results of a chemical examination of the two samples, and seeing that the essential properties of the oil, and notably the viscosities at different temperatures, are substantially identical. The fault of most mineral oils is the great loss of viscosity which they undergo by rise of temperature (as will be seen from the above table), so that an oil which at the ordinary temperature of the air is amply viscous for its purpose, may become altogether too fluid and mobile at the temperature of the bearing which it is used to lubricate. Its viscosity should, therefore, be determined at the maximum temperature that the class of bearing upon which it is to be employed is likely to attain. Besides a suitable viscosity, mineral oils used for lubrication should have a high flashing point, considerably above the maximum temperature to which they are likely to be exposed. Seeing that mineral oils are obtained by processes of fractional distillation, they frequently contain constituents of lower boiling point than that at which the main part of the oil begins to distil, and consequently may possess a low flashing point (see *Petroleum*, Vol. II.). For a lubricant, a low flashing point is injurious, as it involves a greater fire risk, and also occasions waste by evaporation during use. This objection does not arise with fatty oils, for their flashing points are usually high—*e.g.*, 400° to 500° F. = 204° to 260° C. No mineral oil should be used as a lubricant which has a lower flashing point than 150° C. = 302° F.; and when high temperatures have to be provided for, as in cylinder lubrication, still higher flashing points—*e.g.*, 200° to 250° C. = 392° to 482° F.—are requisite. In the foregoing figures the **flashing point** meant is that obtained

by the "close test;"* when the "open test" (identical with the close test, save that the vessel in which it is performed is freely open to the air) is adopted, flashing points from 30° to 60° F. higher than those given by the close test are obtained for the same class of oil. The temperature at which the oil remains ignited **(firing point)** is still higher, the difference being sometimes as much as 100° F. The statement of the flashing point of an oil should, therefore, always be accompanied by a note of the method by which it has been determined.

In a cylinder oil, beside the necessity for a high flashing point, is the requirement that the oil should yield but little matter volatile in a current of steam, lest a portion of it be vapourised with the exhaust steam, and, entering the condenser, find its way into the boiler (p. 106). As it may happen that a portion of the oil is volatile independently of the presence of steam, this quality should also be determined in valuing a mineral oil. The loss at the maximum temperature to which the oil is to be exposed, should not exceed 1 per cent. in six hours. A good mineral lubricating oil should be thoroughly refined, that is free from mineral or organic acid, alkali, and tarry matter. Paraffin wax should be absent, as it separates on cooling, forming a semi-solid magma instead of a highly viscous fluid.

MIXED OILS.—The facts that mineral oils have no tendency to change by exposure to the air, and neither gum nor attack the metal of the bearings, and that fatty oils retain their viscosity fairly well on rise of temperature, have led to the use of mixed oils, which to some extent combine the good qualities of both classes. As, however, they are invariably sold under fancy names, at fancy prices, it is always cheaper and more satisfactory for the user of lubricants, should he need sufficiently large quantities, to buy fatty and mineral oils separately, under proper expert advice, regard being had to the class of bearing to be lubricated; such oils may then be blended by himself. Prominent among mixed oils are cylinder oils and "valvolines," which are intended to carry the heavy pressures and endure the high temperatures that obtain inside a steam cylinder. Heavy fatty lubricants such as tallow, are apt not only to lose a great proportion of their viscosity at these temperatures, but are also split up by the steam in the manner already referred to, and the liberated fatty acids act freely on the metal of the cylinder with which they are in contact, producing masses consisting of the soaps of the heavy metals. These soaps not only block and gum up the moving parts, but are indications of the fact that, to produce them, serious corrosion must have occurred. Very heavy semi-solid mineral oils mixed with fatty oils or with soaps are there-

* This is carried out by heating the oil in a vessel which allows of very limited access of air, and applying a light as the temperature rises, until the vapour from the oil ignites with a slight flash.

fore found to lead to less trouble than fats alone, the corrosion being greatly less, while sufficient viscosity to properly lubricate the moving surfaces is retained. Most fatty oils can be used for improving mineral oils in respect of constancy of viscosity, and even those which become rancid and hydrolyse readily are less liable to those changes when in a mixture, than when used *per se* —the mineral oil exercising a protective influence.

Seeing that the function of the fatty oil added to a mineral lubricant is to raise its viscosity, castor oil is frequently used for this purpose; it is, however, not miscible in all proportions with mineral oil, and its blending is, therefore, effected by the addition of a third oil, such as lard or rape oil. Blown oils, which are prepared from rape or cotton seed oil (see *Oils*, Vol. II.), have a viscosity even surpassing that of castor oil, but their use is not legitimate unless acknowledged.

The use of mineral oils, sometimes of very indifferent quality, or ill-fitted for the purpose to which they are applied, has led to attempts to increase their viscosity, especially at high temperature, by the addition of various substances which may be conveniently known generically as **oil thickeners.**

Mineral oils may be rendered solid or semi-solid by the addition to them of a small quantity of soap, that is the alkali salt of a fatty acid. The "soaps" containing other metals, notably aluminium, combined with a fatty acid, are still more effective. There is a considerable trade in the manufacture of aluminium oleate, stearate, and palmitate, which are generally prepared by precipitating the corresponding sodium salt with alum or aluminium sulphate.

These bodies **(oil pulp)** are dissolved in a small quantity of mineral oil and the product **(oil thickener)** used for the purpose above-named, by addition (in regulated amount) to the oil it is desired to thicken. Unless acknowledged and offered to the consumer without disguise, oils thus thickened must be considered adulterated. Indiarubber, rosin, and similar viscous materials are also employed for the same purpose.

An analysis of such an oil thickener is quoted by Allen:—

		Per cent.
Mineral oil (specific gravity 0·906),		48
Lard oil,		15
Alumina,	Oil pulp,	6
Fatty acids,		30

SOLID LUBRICANTS.—Tallow by itself cannot be considered as a good example of a solid lubricant, as when used alone it is generally for cylinders where the temperature is above its melting point, and it functions merely as an ordinary oil. A better instance of a solid lubricant is afforded by the mixture of tallow and plumbago sometimes used for heavily loaded

journals where the temperature is low enough to allow of the tallow retaining its condition of solidity. Probably the largest use for solid lubricants is for railway carriage axles. Good axle grease consists of a small quantity of soap serving to entangle, render more concrete and thoroughly emulsify a mixture of fat or fatty oil and water. The usual procedure in making these greases is to mix tallow or palm oil, or both, with a liquid fatty oil—such as rape oil—water, and caustic soda or carbonate of soda, the alkali serving to form a small quantity of soap with the fatty acid invariably present in commercial oils and fats, and to act in the manner described above. It needs much skill to procure a good grease of which the constituents will not segregate on exposure to the temperature which it is likely to attain when used as a lubricant—*e.g.*, 150° F. = 65° C. As the fats of which the grease is made melt at a temperature below that which the grease is intended to endure, the amount of soap, and water emulsified by means of the soap, are the chief causes of its satisfying this condition, and it is perfectly possible, therefore, to prepare a grease which is both more costly and less effective than another properly mixed.

Reducing the amount of water very much below 40 per cent. is apt to cause the fat to segregate when the grease is heated, and the grease to fuse as a whole at a temperature below that normal to a grease of good quality. On the other hand, increasing the water much above 50 per cent. robs the grease of some of its lubricating power, and is, moreover, unless provided for by a lower price, a fraud. For common purposes, especially for outdoor work, such as the greasing of trolly axles, rosin grease is used. It consists of rosin oil (see *Destructive distillation*, Vol. II.) treated with slaked lime, which converts it into a pasty mass of fair lubricating qualities. Rosin oil is composed of a number of unsaturated hydrocarbons, some of which have the property of combining with the hydroxides of the alkalies and alkaline earths; the resin acids generally present in rosin oil doubtless contribute to this result. The compound thus formed can emulsify a large excess of rosin oil, so that commercial rosin grease may contain over 96 per cent. of its weight of rosin oil. Barium sulphate, kaolin, calcium carbonate, and black lead are often added as make-weights, and, if gritty, are not only diluents, but also actively objectionable. Soapstone would be a more reasonable addition. The following percentage composition is that of a typical railway grease:—Water 50, tallow 30, palm oil 10, sodium carbonate 10.

CORROSION INDUCED BY LUBRICANTS.—Corrosion is induced by the presence of free fatty acids in fatty oils and in admixtures of these with mineral oils; it increases, though perhaps not in direct ratio, with the percentage of free fatty acid. Oils, whether fatty or mineral,

imperfectly refined and containing in consequence free mineral acid, or sulphonates which are readily split up into acid products, will also give rise to corrosion.

"Brass" bearings—that is, bearings made of gun metal or similar alloys—are often severely attacked by an acid lubricant, while iron and steel are less affected, and white metal bearings suffer least of all. A lubricant containing an appreciable amount (over 4 per cent.) of free acid before being put into use, should not be tolerated. Those containing fatty oils may, although originally neutral, develop fatty acid (p. 116), and their conditions of use may be such that this alteration is inevitable. The development of acidity in oils is of considerable importance in modern engineering practice, inasmuch as most large users of lubricants arrange to supply a continuous stream of oil to all heavily loaded bearings that must be kept cool, and recover the oil, filter it, and use it again. Mere filtration will not affect its acidity, and if of a nature to become acid, it should be freed from acid at intervals by treatment with caustic soda, or rejected altogether, and a new supply procured after due analysis.

PART II.

METALLURGY.

METALLURGY deals with the treatment of metalliferous minerals (ores) for the purpose of winning the metals which they contain, and with the subsequent purification of the crude metal first obtained. For convenience, metallurgical processes may be regarded as falling into two classes, dry and wet, the former including those in which advantage is taken of the reactions which occur at high temperatures, and the latter dealing with those dependent on such reactions as take place in aqueous solution.

A. **METALLIFEROUS ORES.**—Comparatively few of the metals are found native—*i.e.*, in the metallic state—either approximately pure or alloyed with some cognate metal; the majority of them occur in the form of true ores, which are compounds of metals with non-metallic elements. The following classification includes most of the common ores:—

(1) As metals—Copper, bismuth, mercury, silver, gold, platinum and its congeners. Silver and gold are found alloyed.
(2) As oxides—Iron, copper, tin, zinc, manganese and aluminium.
(3) As sulphides—Lead, copper, zinc, antimony and mercury.
(4) As carbonates—Copper, zinc, lead and iron.
(5) As haloid salts—Silver, aluminium and sodium.
(6) As arsenides and antimonides—Nickel* and cobalt.

It must not be supposed that commercial ores are usually pure substances of fixed composition, like those to which they are referred in the foregoing list. Pure specimens of each of the compounds exist, but are too rare to form a source of the metal. The ease with which metals replace each other in minerals, leads to the existence of ores which, although referable to one of the above classes, contain two or more metals. Thus, unmixed sulphides of copper are far less common than copper pyrites, which contains both sulphide of copper and that of iron. Ores are associated with valueless earthy matters—*e.g.*, oxides,

* Also found in large quantities as a double silicate of nickel and magnesium.

carbonates, and silicates of difficultly reducible metals, such as aluminium, calcium, and magnesium (also with silica as quartz). The necessity for the separation of this **gangue** before the mineral can be profitably reduced to metal, much diminishes the value of the ore.

B. **METALLURGICAL PROCESSES.—DRESSING (Sizing and Concentration).**—This consists in partially freeing the ore from gangue by mechanical methods, and comprises hand-picking, to remove large lumps, followed by reduction to coarse powder and separation by **levigation.** This latter process consists in washing the crushed ore, the pieces of which should be of as uniform size as possible, with a stream of water (or in some cases air), the gangue being carried away and the heavier ore left; the separation depends on the size of the particles as well as their specific gravity. For an illustration of mechanical dressing, the treatment of tin ore, which will be dealt with in its own section, may be quoted. Where the ore is magnetic, it is possible to separate it from the gangue by washing the crushed ore between the poles of a magnet.

EXTRACTION.—Both wet and dry methods of extraction are in use, the former being the more recent and in many cases more rational; speaking generally, however, wet processes have not been brought to such comparative efficiency as the dry methods, which have the advantage of centuries of experience in their working. The only essential process common to wet methods is the leaching out of the metal by means of a suitable solvent. To render this possible, some preliminary treatment is frequently necessary, to convert the metal into a soluble salt; for example, the treatment of silver ores by the Augustin process (*q.v.*). The subsequent extraction of the metal from the solution is specific for each case, and no general principles can be conveniently laid down. In dry processes, however, certain general methods can be distinguished—viz., roasting (calcination), reduction, and refining.

Roasting and Calcination.—The object of these processes is generally the elimination of sulphur, arsenic, carbon dioxide, or bituminous matter from the ore. In the case of sulphur and arsenic, these are removed in roasting by oxidation, SO_2 and As_4O_6 being volatile. Carbon dioxide is simply removed in calcination by the dissociation of the carbonate containing it; bituminous matter is also burnt away during the process, itself serving as the fuel. The operation is sometimes still conducted in heaps which consist partly of the fuel and partly of the ore; sometimes in stalls, which are rectangular spaces enclosed on three sides by brick walls and open at the front and top, the former being closed by a temporary wall after the introduction of the charge. More generally, some form of reverberatory furnace is used, as the roaster; muffles—*e.g.*, for blende—may be

used, and various contrivances for continuous roasting, which will be spoken of individually. The product is usually a more or less pure oxide of the metal.

Reduction (including fluxing).—By reduction is meant the obtainment of the metal as such from the ore. Since the preliminary roasting has converted the ore into an oxide, the subsequent reduction consists in removing the oxygen by hot carbon or carbon monoxide. In order that the separated metal may agglomerate, it is frequently necessary to render fluid residual gangue by the addition of some **flux**—*i.e.*, a substance capable of forming a fusible slag with the said gangue. The nature of this flux depends on that of the gangue, and is either "acid" (*e.g.*, SiO_2) or "basic" (*e.g.*, CaO), according as the gangue is basic or acid. Reduction is generally effected by the direct action of carbonaceous fuel, or by means of carbon monoxide in a reverberatory furnace. There is, however, a certain class of ores which is capable of "self-reduction"—*i.e.*, of requiring the introduction of no extraneous reducing agent. In such ores the sulphur occurring as sulphide in one portion may be used to remove the oxygen existing as oxide from another portion, the metal from each being thus freed. Ignoring secondary reactions, the following equation will represent a case of this kind :—

$$2PbO + PbS = 3Pb + SO_2.$$

Refining.—This term is applied to the removal of impurities from the crude metal obtained by reduction. Refining by oxidation generally consists in partially oxidising the metal by roasting in a current of air, whereby the more readily oxidised impurities are oxidised and either volatilised or removed as slag. Examples of this are the refining of crude copper and the puddling and bessemerising of iron. A variation consists in using some of the oxide of the metal as the oxidising agent, instead of, or supplementary to, air. When this process is adopted, it is frequently necessary to correct the refined metal, which itself has become slightly oxidised, by a secondary reduction process; the "poling" of copper serves as an example. This process is not applicable to the removal of impurities less oxidisable than the metal to be refined—*e.g.*, silver from copper. Refining by **liquation** depends upon the difference between the melting point of the metal to be purified and those of its impurities. The metal is exposed to a temperature just sufficient to melt it and to cause it to flow away from the less fusible impurities. Thus, crude tin is eliquated from its impurities, such as iron and copper. Another general principle of which advantage is taken in refining, is that involving the use of immiscible solvents. This process, which consists in extracting a substance dissolved in one liquid by means of another liquid in which the substance is more soluble, the two liquids

being immiscible (for a parallel case the extraction of iodine from its aqueous solution by means of carbon disulphide may be quoted), is exemplified by the Parkes process of desilverising lead. The argentiferous lead is fused and treated with zinc, which is nearly insoluble in lead, and is at the same time a better solvent for silver than is lead. The zinc, containing silver, floats on the surface, and is skimmed off. A similar method is that of "settling out," in which one metal is allowed to subside, by reason of its higher specific gravity, from another in which it is immiscible, the two layers being then separated.

One other process of obtaining fairly refined metals, and that directly from the ore, is of sufficient importance to deserve separate mention; it consists in distilling the ore, if necessary previously roasted to oxide, with carbon. Mercury, cadmium, and zinc are thus obtained. With the increased use of the extremely high temperatures attainable by the electric furnace, it is not improbable that this method may be extended to the winning of metals less volatile than these three.

IRON.

Although iron is one of the most widely diffused elements, it is only sufficiently abundant in certain distinct ores to be worth working. The characteristic red, brown, or yellow colour of ferric oxide in the anhydrous or hydrated state, proclaims the presence of iron in many soils and rocks, when the actual quantity contained therein is relatively inconsiderable. Thus, reddish sandstones and sands containing iron oxide are common enough, but the proportion of iron is far too small to render it profitable to remove the siliceous impurity which forms the bulk of the material.

Native iron (iron in the metallic state) occurs too rarely to be of any commercial importance. Some meteorites are chiefly composed of iron, as may be seen from the following typical example:—

	Per cent.
Iron,	90·88
Nickel,	8·45
Cobalt,	0·66
	99·99

Globules of metallic iron have been found in basalt and other igneous rocks, and occasionally fused masses of iron are found in coal measures.

ORES.—Oxides of Iron.—The most important of these are the ores known as hæmatites from the fact that certain varieties have a blood-red colour. Two classes are distinguished, the

first, red hæmatites, are anhydrous ferric oxide, the others, brown hæmatites, being hydrated.

The former contain up to 70 per cent. of iron (this being the percentage in pure Fe_2O_3). They are usually associated with earthy matters, so that this percentage is reduced to 60 to 65 per cent. Red hæmatite proper is known as **kidney ore** from the shape of the pieces in which it is found; it has a fibrous structure, a dull red colour, and specific gravity about 5·0.

Specular Iron Ore, a crystalline variety, is so called on account of its mirror-like lustre; it is dark grey, but when powdered is red. Both these forms are widely distributed in the United Kingdom. There are also notable deposits of hæmatite at Bilboa in Spain and in the United States, whilst specular iron ore occurs in the Island of Elba and in Brazil.

The brown hæmatites (**limonite**) contain, when pure, $2Fe_2O_3.3H_2O$, which corresponds with a content of 60 per cent. of iron, though the ores actually worked rarely contain much more than 50 per cent. Northamptonshire and Spain are the chief sources of brown hæmatite for iron making in this country. A special variety of industrial importance is **bog-iron ore** used for the purification of gas (see *Destructive distillation*, Vol. II.). The following analyses give the composition of typical red and brown hæmatites :—

	Red Hæmatite.	Brown Hæmatite.
	Per cent.	Per cent.
Fe_2O_3,*	90·36	80·80
MnO,	0·10	1·13
Al_2O_3,	0·37	...
CaO,	0·71	2·48
MgO,	0·06	...
P_2O_5,	Trace	...
FeS_2,	0·06	...
Insoluble siliceous residue,	8·54	5·55
Water and volatile matter,	...	8·98
	100·20	98·94
* Corresponding with metallic iron,	63·25	56·56

The only other oxide of iron of importance as an ore, is the **magnetic oxide** (*magnetite*) the typical formula of which is $FeO.Fe_2O_3$, although the proportion of FeO to Fe_2O_3 may vary from the ratio 1 : 1 (which corresponds with 72·5 per cent. of metallic iron). The proportion of the iron is, however, generally considerably smaller than is indicated by this formula, from the presence of siliceous and earthy matter, as is shown by the following analyses :—

	1	2
	Per cent.	Per cent.
Fe_2O_3, FeO, *	62·06	44·40
	28·42	20·00
MnO,	...	0·16
CaO,	Trace	0·60
MgO,	1·44	1·00
Al_2O_3,	Trace	5·20
P_2O_5,	...	0·50
Sulphur,	0·07	Trace
Insoluble siliceous matter	7·60	24·20
Water,	...	2·50
	99·59	98·56
* Corresponding with metallic iron,	65·60	46·63

Carbonate of Iron (*Spathic Iron Ore*).—The pure mineral is ferrous carbonate, $FeCO_3$, and contains 48·2 per cent. of Fe; it is usually associated, however, with carbonates of manganese, lime, and magnesia. It is not very abundant in the United Kingdom, the chief localities being in Durham and Somersetshire; on the Continent it is more abundant, notably in Styria. Its freedom from phosphorus makes it suitable for the manufacture of certain classes of steel. The following analyses exhibit its composition:—

	Somersetshire.	Styria.
	Per cent.	Per cent.
FeO, Fe_2O_3, *	43·84	55·64
	0·81	...
MnO,†	12·64	2·80
CaO,	0·28	0·92
MgO,	3·63	1·77
CO_2,	38·86	38·35
H_2O,	0·18	...
Insoluble matter,	0·08	...
	100·32	99·48
* Corresponding with metallic iron,	34·67	43·27
† Corresponding with metallic manganese,	9·80	2·17

Clay ironstone is ferrous carbonate associated with clay and sand. It is the most abundant English ore, and occurs in the coalfields of Wales, the Midlands, and Scotland. A variety of clay ironstone is **black-band** ore, which contains much carbonaceous matter, whence its name. The celebrated Cleveland ore is a clay ironstone which is poor in manganese, but rather richer in phosphorus than are most other ores of this class. Clay ironstones are also found in strata containing coal, limestone, and fireclay; all these materials are required in iron manufacture.

The following are partial analyses of clay ironstones:—

	Clay ironstone (from Yorkshire).	Scotch Blackband.	Cleveland ore.
	Per cent.	Per cent.	Per cent.
FeO, Fe_2O_3, *	35·38	53·82	39·92
	1·20	0·23	3·60
MnO, ...	0·94	...	0·95
CaO, ...	2·78	1·51	7·44
MgO, ...	2·22	0·28	3·82
SiO_2, ...	...	2·00	7·12
CO_2, ...	25·41	34·39	22·85
P_2O_5, ...	0·48	...	1·86
Carbonaceous matter, . .	0·23	7·70	Trace
* Corresponding with metallic iron, ...	28·76	41·60	33·62

Sulphide of Iron.—Iron pyrites, FeS_2, is never directly smelted, but spent pyrites from vitriol making (*q.v.*, Vol. II.) is occasionally used as a source of iron.

PRINCIPLES OF IRON EXTRACTION.—Where a pure oxide of iron is attainable, a malleable (approximately pure) iron can be prepared by direct reduction with charcoal. This is still practised where charcoal is cheap, and pure magnetite, &c., abundant. This reduction is probably effected according to the equation:—

$$Fe_3O_4 + 4CO = Fe_3 + 4CO_2.$$

The pure iron thus reduced, although infusible at ordinary furnace temperatures, is obtained in a partly agglomerated state, the particles not being separated by foreign siliceous matter. In the case of an ordinary ore containing argillaceous or siliceous matter, such agglomeration does not take place unless the clay, &c., be fluxed by the addition of limestone, which forms fusible silicates—slag—therewith. The scarcity of charcoal in this country necessitates the use of a fuel with a high content of ash (viz., coke); the presence of this ash, which is siliceous, also demands a basic flux. The impurities in the ore and fuel introduce sulphur, phosphorus, and silicon into the iron, and a portion of the carbon of the fuel is also taken up, the resulting crude iron being more fusible than the pure metal, and, therefore, running together as a liquid instead of agglomerating as a paste—a condition which renders continuous working practicable. The application of these principles will be dealt with under appropriate headings.

PREPARATION OF THE ORE FOR SMELTING.—In order to expose as large a surface to the reducing gases of the blast furnace (*v.i.*) as is compatible with the free passage of the blast between the fragments of ore, the ore is crushed, in

most cases to about 2-inch cubes. The crushing is effected by ordinary stone-breakers, or by crushing rolls.

The removal of gangue **(concentration)** by hand-picking is occasionally practised, and **magnetic separators** have been used with success. The method of magnetic separation consists essentially in sizing the ore by means of sieves, and passing it between the poles of powerful electro-magnets, which retain magnetic oxide, and allow free passage for the gangue. The plan can be used for magnetites, or for hæmatites previously reduced to the intermediate stage of oxidation, and thereby rendered magnetic.

Most iron ores, save those which are free from volatile constituents—*e.g.*, magnetites and red hæmatites—are roasted before being reduced. This is done either in open heaps, which consist of a pile of ore and small coal (except in the case of blackband, which contains its own fuel), or in rectangular enclosures, the walls of which are 6 to 12 feet in height. The combustion of the heap is started by brushwood. Various kilns, heated by solid fuel or producer gas, or in some cases by the waste gas of the blast furnace, are also used for roasting. The advantages of roasting are—(1) the expulsion of volatile constituents—*e.g.*, water, CO_2, sulphur, and arsenic—and *pari passu* the concentration of the ore and of the waste gases from the blast furnace (*v.i.*); (2) the rendering of the ore more porous, and consequently more permeable by the reducing gases of the blast furnace; and (3) the oxidation of Fe″, which forms a stronger base than Fe‴, and, therefore, tends to pass into the slag as silicate.

REDUCTION OF THE ORE IN BLAST FURNACES.—The modern blast furnace is a masonry tower, A (Fig. 13), 80 feet high, lined with firebrick, the interior of which is so built that it is of the form of the frustra of two cones base to base; the upper frustrum, B, constituting about three-fourths of the total height, is called the **stack** or **body**; the lower frustrum, C, is termed the **boshes.** The diameter across the boshes (the **belly**) is about 24 feet. The lowest portion of all, D, is the **hearth** or **crucible,** and is about 8 feet in diameter. The upper end, or **throat,** of the furnace is closed by a cast-iron cup and cone, E, to allow of charging without interfering with the exit of the gases through the pipe, F. At the bottom of the hearth a space, G, is left in the brickwork, which can be tamped up while the fused metal is collecting, and unstopped when the charge is ready to be drawn. To avoid the fluxing action of the slag, the firebrick lining of the boshes is sometimes replaced by bricks of graphitic coke, which are, however, liable to wear and tear by oxidation. On account of the high temperature needed for the smelting of iron, large volumes of air at a considerable pressure have to be supplied to induce sufficiently rapid combustion; it is obvious that, within certain limits, it is advantageous to heat

the blast. The air is supplied from a blowing engine, through the pipe, H, which nearly surrounds the boshes, and is provided with a number of jets, K, called the **tuyères (twyers)**, which pass into the furnace at the upper part of the hearth. The nozzles of the twyers are protected from the heat of the hearth by a jacket through which cold water is circulated. The air supply is heated by passage through the **Cowper stove**, L. This consists of a

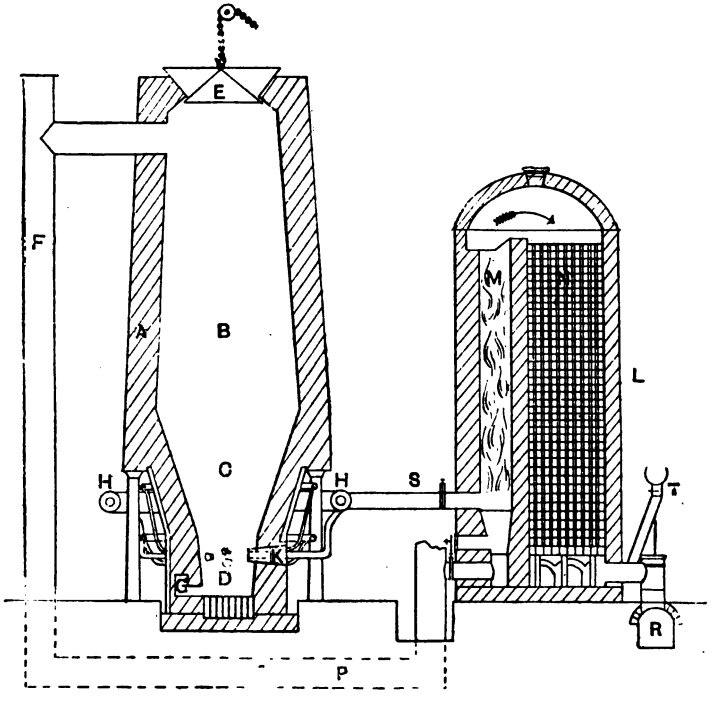


Fig. 13.—Blast furnace.

A, Masonry tower; B, body; C, boshes; D, hearth or crucible; E, cup and cone for closing throat; F, exit pipe; G, tapping hole; H, air-supply pipe; K, twyers; L, Cowper stove; M, flue; N, chequer firebrick; P, underground pipe; R, flue to chimney; S, T, air pipes leading to twyers.

tower containing a flue, M, the remainder being filled with chequer firebrick, N. The object of this stove is to utilise the heat of the gases from the blast furnace, as well as that produced by the combustion of the CO, &c., contained in them. Their value as a fuel may be judged from the following analysis, which is from a Cleveland furnace fed with coke :—

	Per cent.
N,	54·91
CO_2,	18·36
CO,	26·66
H,	0·07
	100·00

The gases from the blast furnace pass by an underground pipe, P, into the flue of the stove, where they meet a supply of air and are burnt, the products of combustion travelling down through the chequer brickwork, N, to which they impart their sensible heat, before passing away to the chimney by R. These stoves are worked in sets, one being heated in the manner described above while another is serving to heat the air blast, which is forced in the contrary direction through the pipes, S, T, to the twyers. The pipe P thus serves to feed all the stoves. Formerly the blast was heated by passage through cast-iron pipes, set in a furnace fed by the combustible gases from the blast furnace—a method which allowed of continuous working with a single stove—but the need of higher temperatures made cast iron an unsuitable material for the construction of the stove, and simple substitution of a fireclay for a cast-iron tube was impracticable, owing to the difficulty of keeping it tight to the pressure of the blast (2½ to 7 lbs. per square inch), and a plan whereby the air was heated by direct contact with a mass of refractory material had to be adopted. A modern hot blast has a temperature of about 800° C. = 1,472° F. Where blast furnaces are worked with raw coal instead of coke, the condensable products of the destructive distillation of the fuel (notably tar and ammonia) are collected before the gas is burnt in the stoves. This is effected either by passing the gases through an air condenser and water scrubber, similar to those used in gas manufacture (*q.v.*, Vol. II.), or by treating the gases with a shower of sulphuric acid, both methods involving the cooling of large volumes of gas. To avoid this it has been proposed to mix the blast furnace gases with SO_2 from pyrites kilns, and to collect the resulting ammonium sulphite. By the first-mentioned method about 40 gallons of crude tar and 24 lbs. of ammonium sulphate per ton of coal are obtained.

In starting a blast furnace, the temperature must be slowly raised, to avoid cracking the walls of the structure. The hearth is filled with wood, and the boshes with coke. When this fuel has been ignited, the body of the furnace is filled with ore, limestone, and fuel (constituting the **burden** of the blast furnace), the materials being charged in rotation. The proportions of these materials vary according to the character of the ore and according to other conditions. The blast is gradually turned on, and after about three weeks the furnace is working at full blast.

The rotation of charging is maintained until the furnace needs repair, crude iron and slag collecting at the bottom and being periodically tapped. The slag, which collects above the molten iron, is run into waggons, whilst the metal is allowed to flow into **pig-moulds** fashioned in sand to receive it. The selection and proportion of the materials to be used as flux are determined by the nature of the iron to be produced (*v.i.*), as well as upon the character of the gangue. A good blast-furnace slag must contain silica, alumina, and lime. When the gangue is chiefly argillaceous, limestone suffices as a flux; but if it be siliceous, an aluminous ore must be added; while if it be basic—*e.g.*, in spathic or oolitic ore, which contains calcium carbonate—both silica and alumina, as clay or shale, are required. A judicious mixing of ores will frequently serve the same purposes. The most siliceous slag usually made corresponds with the general formula $2RO.3SiO_2$, where RO is any base, either RO or R_2O_3. The most basic blast-furnace slags correspond with the formula $10RO.3SiO_2$. The average coke-fed furnace slag approximates to $2RO.SiO_2$. Thus the selection of the fluxing material must depend upon the analysis of the ore and of the flux itself, and on the requirements of each particular blast furnace and its produce. Analyses of a few typical slags are given below:—

	Grey Iron (Cleveland).	White Iron (Dowlais).
	Per cent.	Per cent.
SiO_2, . . .	43·07	29·92
Al_2O_3, . .	14·85	21·70
FeO, . . .	2·53	0·32
MnO, . . .	1·37	0·80
CaO, ...	28·92	38·72
MgO, . . .	5·87	6·10
K_2O, . . .	1·84	...
CaS, . . .	1·90	...
P_2O_5, . . .	...	0·07
S, . . .	...	1·61

Blast furnace slag is a crude glass, sometimes opaque, and varying in colour from dark grey to light green. Slags, when acid, are permanent in air like glass, but when basic may disintegrate spontaneously by the hydration of the lime which they contain. Blast furnace slag is practically a wasted product, but a small quantity is used as ballast for paving, for cement making (*q.v.*, Vol. II.), and for making **slag wool**. This material is prepared by scattering a stream of slag into tenuous filaments by a jet of air. It resembles glass wool in appearance, but is even more brittle, and finds application as a lagging material.

Coke is preferable to coal in the blast furnace, as it contains a smaller proportion of sulphur. Good blast-furnace coke should

contain not more than 3 per cent. of moisture, 10 per cent. of ash, and less than 1 per cent. of S. It should be dense and silvery in appearance, and have an apparent density (including pores) of 0·8. Its mechanical strength should be sufficient to bear the burden of the blast furnace, and it should be capable of resisting oxidation and combustion until at the temperature of the hearth of the blast furnace.

The limestone should be non-dolomitic, and is preferably used without previous burning, as when caustic lime is charged it becomes carbonated at the throat of the furnace and has to be reburnt lower down the body. The raw materials and products of a Cleveland blast furnace are given as follows by Turner:—

Raw Materials.	Cwts.	Products.	Cwts.
Calcined iron stone,	48	Iron,	20
Limestone,	12	Slag,	30
Durham coke,	20	Waste gases,	130
Air,	100		
	180		180

The changes which occur in the reduction of iron in the blast furnace are mainly influenced by the temperatures which obtain in the various parts of the furnace. These changes comprise the reduction of oxide of iron to metallic iron, the causticising of the limestone, the reduction of a portion of the carbon monoxide to carbon by the action upon it of the iron already reduced, the combination of carbon and iron to form carburetted or cast iron (which is more fusible than the pure spongy iron first produced), and the union of the lime with the gangue to form slag. Attempts have been made to map out the interior of the blast furnace into "zones," appropriate to certain reactions. According to this method of explanation the ferric oxide is reduced near the throat of the furnace at the point where the temperature has reached dull redness, the change being effected by the reducing action of carbon monoxide—which constitutes at this point about one-third of the total gases, and has been produced by the reduction of CO_2 generated by the fuel in the lower part of the furnace. Spongy iron disseminated through gangue results, and as it descends into the body of the furnace it is partly oxidised by more CO (which is capable, according to the temperature, of acting as an oxidising and as a reducing substance) with the liberation of carbon. Doubtless the ferrous oxide is again mainly reduced before fluxing as but little iron appears in the slag. The finely-divided carbon and iron unite to form fusible carburetted iron which is melted in the boshes at the same time as the fluxing of the gangue takes place. The causticising of the limestone occurs at a point rather below that at which reduction of iron oxide begins.

The powerful reducing atmosphere of the blast furnace and the high temperature obtaining therein, cause the reduction of other substances than iron, chiefly manganese, silicon and phosphorus, while sulphur (mainly from the fuel) is retained unoxidised, and appears together with the above-mentioned bodies in the crude iron. On account of the simultaneous presence of a high temperature, basic material (alkalies from the ore, &c.), carbon and nitrogen, alkali cyanides are produced in the normal working of the blast furnace. The quantity of cyanogen thus escaping may amount to 6 grms. per cubic metre of the waste gases. When titanium is present in the ore (*e.g.*, as TiO_2 in clay) nitrogen is fixed as nitride as well as cyanide, large crystals of the compound $TiCy_2.3Ti_3N_2$ being produced. These constitute infusible masses, called "bears," in the blast furnace, and much impede the working.

The limit to the efficiency of a blast furnace regarded as a heat-machine appears to be determined by the fact that carbon monoxide ceases to be efficient as a reducing agent for ferric oxide, at the temperature obtaining at the throat of the furnace, when it is so diluted with CO_2 that the ratio of the carbon which they respectively contain falls below 2 : 1. Thus the difference between the heat produced by the combustion of carbon to CO_2 and of carbon to CO (viz., 5,600 Cal. per kilo.) is lost so far as the furnace is concerned, but is largely recovered by the use of the hot blast stove.

About 40 per cent. of the total quantity of heat in the blast furnace is consumed in reducing the iron to the metallic state, 10 to 12 per cent. in the fusion of the iron, and 12 to 15 per cent. in the fusion of the slag, the balance being accounted for by the reduction of impurities, the causticising of the limestone, the reduction of CO_2 from the limestone to CO, and the carburising of the iron, while another large item (about 10 per cent.) is the heat going away with the waste gases; this, however, is mostly recovered.

About 75 per cent. of the total calorific value of the fuel is realised in the blast furnace, on which account it may be reckoned an efficient machine.

The crude iron produced is run from the furnace into sand-moulds, producing **pig iron**; here a portion of the carbon taken up by the iron in the furnace separates from solution in the metal in the form of graphite. A portion of this graphite floats to the surface of the metal as "kish," the remainder being still associated with the metal itself.

When the bulk of the carbon thus separates, the metal is known as **grey** iron; when partial separation takes place **mottled** iron is produced; while when the separation is at a minimum the material is called **white** iron. The production of grey iron occurs in those furnaces which work with siliceous

ores and a high percentage of fuel at a high temperature; silicon is then present in the pig, and induces the crystallisation of the carbon as graphite. White iron, on the other hand, is made in heavily burdened furnaces, working with the minimum of fuel, and contains but little silicon, on which account the separation of graphite does not take place.

The composition of grey and white cast iron is given below :—

	Grey.	White.
	Per cent.	Per cent.
Graphitic carbon, ...	3·30	...
Combined carbon, ...	0·20	3·20
Silicon, ...	3·50	0·64
Phosphorus, ...	0·98	1·32
Sulphur, ...	0·02	0·20
Manganese, ...	1·58	0·60
Iron (by difference), ...	90·42	94·04
	100·00	100·00

White iron is principally used for the production of malleable iron. For this object it is advantageous that it should contain as little carbon as possible and have a low content of silicon, phosphorus, and sulphur. Its specific gravity is 7·5, as against 7·1 for grey iron. It is harder and more brittle than grey iron and somewhat more fusible. Grey iron is used for foundry purposes and steel making. The classes of grey iron richer in graphitic carbon are better mixed with poorer varieties when used for castings. It is this need for mixing which makes casting directly from the blast furnace undesirable, apart from question of convenience. For foundry work the metal is melted in a cupola furnace—a small intermittently worked blast furnace—into which pigs and coke are fed. The oxidation of silicon would occur in this furnace to the detriment of the casting, were it not prevented by manganese, which is the first impurity to be oxidised when crude iron is remelted.

By varying the working of the blast furnace, the crude iron may be made to contain varying proportions of sundry metallic, as well as non-metallic, impurities, whereby its character is much modified. Thus, pig iron rich in silicon (**ferro-silicon**), constitutes a light coloured "glazy" iron useful in the cupola for producing grey iron from white pig. By reducing manganiferous ores in a blast furnace, various grades of manganiferous pigs are made. The presence of manganese causes the crude iron to contain more carbon than does normal pig, the alloy having a

crystalline structure and lustrous appearance, justifying its name **spiegel-eisen** (mirror-iron).

Spiegel-eisen contains about 10 per cent. of manganese, and when this proportion is largely increased (with a practicable maximum of 85 per cent.) the metal is called **ferro-manganese.** Both grades are used in steel making (*v.i.*). Ferro-chromium, made by reducing chrome iron ore, contains 60 to 70 per cent. of chromium, and is also used in steel making. Phosphoric pig iron, containing as much as 7 per cent. of phosphorus, is manufactured for the basic steel process from ores rich in phosphorus, or by the addition of basic slag to the charge.

The fact that graphitic iron (grey iron) is readily convertible into carburetted iron (white iron) by rapid cooling (which prevents the separation of graphite), allows of the production of chilled castings by pouring molten grey iron into moulds, which are constructed of massive iron, at such points of the casting as are to be chilled. The surface immediately in contact with the cold iron is converted into hard white iron to the depth of $\frac{1}{8}$ inch or more. This method is used for rolls and railway carriage wheels, the latter being employed in American engineering practice (*cf.* p. 14).

Pig iron from the blast furnace is of low tensile strength (about 7 tons per square inch) and comparatively brittle. At the same time it is not malleable and cannot be welded. Thus, while cast iron has the special application indicated by its name, its value for structural uses, where tensile strength and ductility are required, is small.

In early days and among primitive peoples, pure iron was reduced directly from the ore, the production of fusible impure iron, such as is obtained from the blast furnace, constituting a later stage of development. The direct production of iron is only practicable, as has been already mentioned, from pure ore (*e.g.*, rich magnetite) and pure fuel—viz., charcoal. The modern large demand for structural iron of high tensile strength, renders it impossible to obtain a sufficient supply from these comparatively scarce materials. Hence it is necessary to produce a crude metal, and to refine this to the desired degree of purity.

For the better realisation of the relation between crude iron and the products of its purification, the following method of classification, which is based on that which is official in Germany, may be quoted (*Ost*):—

Crude Iron	Malleable Iron
Contains over 2·3 per cent. of impurities; generally 9 to 10 per cent. (C, 2 to 5 per cent., together with Si and P) melts without passing through any well-marked pasty stage, is therefore not malleable; brittle at the ordinary temperature.	Contains a smaller proportion than 2·3 per cent. of impurities, chiefly carbon, generally under 1 per cent.; higher fusing point than crude iron, increasing as the impurities decrease; softens gradually on heating up to its fusing point, and is therefore malleable. Those kinds which are markedly poor in impurities are malleable when cold.
A. Grey Iron.—The bulk of the carbon is graphitic, giving a grey fracture.	A. Puddled Iron.—Prepared in a pasty, imperfectly fused state, therefore not homogeneous; contains intermixed slag. Varieties containing more carbon are termed puddled steel.
B. White Iron.—The bulk of the carbon is combined, and is not present as graphitic carbon.	B. Ingot Iron (mild steel).—Prepared perfectly fluid, therefore homogeneous and free from slag. The harder varieties, containing more carbon, may be called ingot steel.*
C. Spiegel-eisen and Ferro-manganese.	C. Special varieties, including malleable cast iron and temper steel—*e.g.*, cementation steel.

The essential difference between **cast iron, steel,** and **wrought iron** (using these terms in their common acceptation) lies in their varying content of carbon. Ideal cast iron consists of Fe with 3 to 5 per cent. of C as graphite; ideal steel of Fe with 0·5 to 2·0 per cent. of combined C; ideal wrought iron of Fe with under 0·1 per cent. of C. Intermediate percentages of C give products approximating to one or other of the materials thus classified. From this it follows that ideal cast iron and ideal wrought iron, when mixed in suitable proportions, would yield steel if the appropriate change in the condition of the carbon were effected. With commercial metals the production of steel by the mixture of cast and wrought iron is generally impracticable on account of the presence of impurities —*e.g.*, phosphorus—which, although of small account in cast or wrought iron, are highly deleterious to steel. The production of steel, therefore, involves more roundabout methods than would appear from its mere percentage of carbon. These will be described in due course.

PURIFICATION OF CRUDE IRON.—Most of the impurities of crude iron, notably carbon and silicon, are more easily oxidisable at high temperatures than is the metal itself, whence it follows that all processes of purification, except that by electrolysis, depend on the removal of the impurities by limited and regulated oxidation, which may be effected either partly by solid

* Used for large steel castings.

oxidants—*e.g.*, in puddling—or by air, as in the Bessemer process. The carbon is removed as gaseous oxides, the silicon as SiO_2, and the phosphorus as P_2O_5, the last two acid oxides being more readily eliminated in the presence of a strong base—*e.g.*, FeO or CaO.

1. **Purification without Complete Fusion of the Product.**—As has been stated above, white iron is better adapted than grey for conversion into malleable iron by puddling, because its comparatively low content of silicon causes it to pass through a pasty stage before fusion, the advantage of which will be gathered from the description of the puddling process (*v.i.*). Grey iron melts more sharply than white, and, therefore, can be oxidised by a gaseous oxidant injected through it more readily than by treatment with a solid oxidant. Oxidation with air blown through the metal is comparatively modern, wherefore the production of malleable iron from grey iron was formerly necessarily preceded by the conversion of the grey iron into white iron. This process was conducted in the refinery—the term being a misnomer as the product is not sensibly refined but merely converted into white iron. The German phrase *weissmachen* (whitening) is more appropriate.

The **refinery hearth** consists of a rectangular cast-iron bed, the floor of which is of sandstone, and the sides hollow and water-cooled. A chimney surmounts the hearth, and upon the latter air is directed through twyers at a pressure of 2 to 3 lbs. per square inch. The floor is protected by a layer of broken sandstone which soon fluxes to a glaze. The charge of grey pig, or of molten iron direct from the blast furnace, mixed with coke, is kept under blast for about two hours, during which time the iron forms a layer beneath the fuel, but is oxidised by the air directed downwards upon it. The silicon is the main impurity oxidised, carbon and phosphorus being but little affected. Thus, the slag is a nearly pure ferrous silicate approximating in formula to $2FeO.SiO_2$. The white iron is run into chilled moulds in the form of plates 2 to 3 inches thick, which are brittle enough to be afterwards easily broken. The refining proper (as distinct from "whitening") of the metal thus obtained was originally effected in an open hearth, which consisted of a forge worked with a blast. In this forge, fuel (charcoal) was first raised to incandescence, and the iron piled on top. After a time the metal melted and trickled through to the bottom of the hearth, passing through the stream of air from the twyer on its way. Basic silicates of iron were thus formed, and a certain amount of decarburation occurred, so that the mass became pasty; it was then balled and replaced on the top of the fuel, its passage to the bottom and oxidation being repeated. Finally, the "bloom," or mass of pasty metal, was beaten under a tilt-hammer to express slag. In this operation oxidation is effected both by solid oxidants (oxides of iron) and by air.

The **puddling process**, introduced about 100 years ago, differs from the open-hearth process, in that the metal is heated by the combustion of gases instead of by direct contact with solid fuel. The solid fuel whence the gases are produced may therefore contain sulphur, the SO_2 given off on combustion not being absorbed by the iron. The need for a non-sulphurous fuel such as charcoal is thereby obviated. The reverberatory furnace shown in Fig. 14 is the oldest form of furnace for this purpose, and provides gaseous fuel in precisely the same manner as the modern gas producer does (see p. 64). The bed of the reverberatory furnace which forms the puddling furnace is of cast-iron plates, supported on wrought-iron bars, which allow of free circulation of air, whereby the plates are cooled. This bed is protected by a lining or "fettling" of hammer slag squeezed from the bloom (*v.i.*), and a superficial layer of nearly pure oxide of iron—*e.g.*, hæmatite, the whole being so moulded that a saucer-shaped depression, is formed. In older forms of the process, known as **dry puddling**, "refined"—*i.e.*, white iron (*v.s.*)—was used and heated until it became pasty and partly oxidised, when it was broken up and continuously stirred to mix it with the oxide formed. In the modern method of puddling—"pig-boiling"—grey iron is used, and allowed to become perfectly fluid before stirring with oxide of iron, which is provided in this case by the fettling. During this incorporation the temperature of the furnace is lowered, and slags containing oxide of iron are added to flux the silica formed by the oxidation of the silicon of the pig. When the blue flame of CO, due to the oxidation of the carbon of the pig

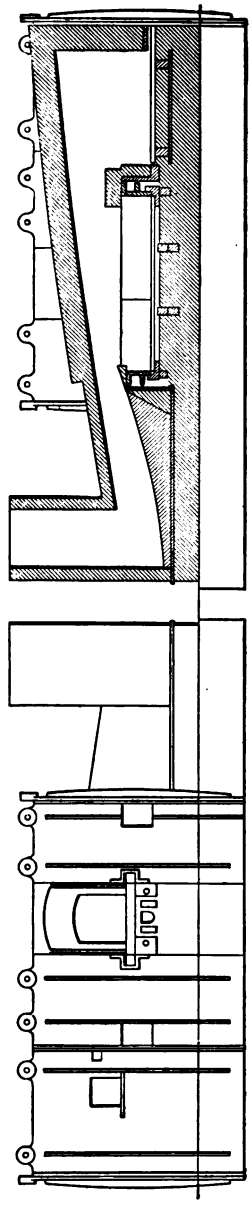


Fig. 14.—Reverberatory furnace (vertical elevation and section).

by the oxide in the slag, is perceived, the temperature is raised, to compensate for the decreasing fusibility of the iron as its impurities are removed. The charge is now "rabbled"—*i.e.*, swept from the centre towards the circumference of the hearth by an iron bar—during which process the ebullition of the mass caused by the escape of CO decreases, and the iron "comes to nature." After another thorough mixture the metal is agglomerated into balls, which are brought to a welding heat and withdrawn from the furnace. It is then strongly compressed either by blows from a steam hammer or by means of a squeezer consisting of a lever, on the principle of a pair of nut-crackers, working against a bed plate. The slag is thus squeezed out, and a "bloom" of wrought iron is obtained which can be rolled down into bars by passage between grooved rollers. The iron is rendered more nearly homogeneous and its quality improved, by cutting the puddled bar into lengths, **piling** it, re-heating in a reverberatory furnace, and again hammering and rolling. For re-heating furnaces gas-producers (with the usual regenerators) are often employed. The iron thus improved is of the grade known as "merchant iron."

Many attempts have been made to replace hand puddling by mechanical processes, but hitherto they have met with very limited success. There are two classes of mechanical puddling processes; in the one the rabble is actuated by power, in the other the bed of the furnace takes the form of a cylinder, heated internally by producer gas from a separate grate, and capable of rotation, the whole arrangement being comparable with the revolving black ash furnace (see *Alkali*, Vol. II.). The cylinder is lined with oxide of iron fettling, which is brought into contact with the charge and effects decarburation. The following analyses (*Turner*) show the composition of puddled bar and of the finished wrought iron:—

	Puddled Bar.	Wrought Iron.
	Per cent.	Per cent.
Carbon, ...	0·10	0·06
Silicon, ...	0·13	0·04
Manganese, ...	0·08	0·08
Phosphorus, . . .	0·35	0·20
Sulphur, ...	0·05	0·05
Iron (by difference), . .	99·29	99·57
	100·00	100·00

The output of wrought iron by puddling crude iron is about 90 to 94 per cent. of the iron charged.

Chemistry of Puddling.—The process of puddling is conducted essentially for the selective oxidation of the impurities of the crude iron, but at the same time the charge must be

mechanically worked, not only to expose ample surface to the incoming air, but to cause the slag (formed by the impurities), which is intimately emulsified with the metal, to run together and agglomerate in distinct drops easy of expression under the hammer. In common with other processes for purifying iron, puddling first causes the elimination of silicon and manganese, carbon, sulphur, and phosphorus being removed at a later stage.

If the removal of carbon from crude iron by puddling be stopped before the stage corresponding with wrought iron is reached, a steely iron, called **puddled steel,** is obtained. A pure raw material must be employed, as the influence of sulphur and phosphorus upon steel is more deleterious than upon wrought iron. Modern steel-making processes have displaced this method.

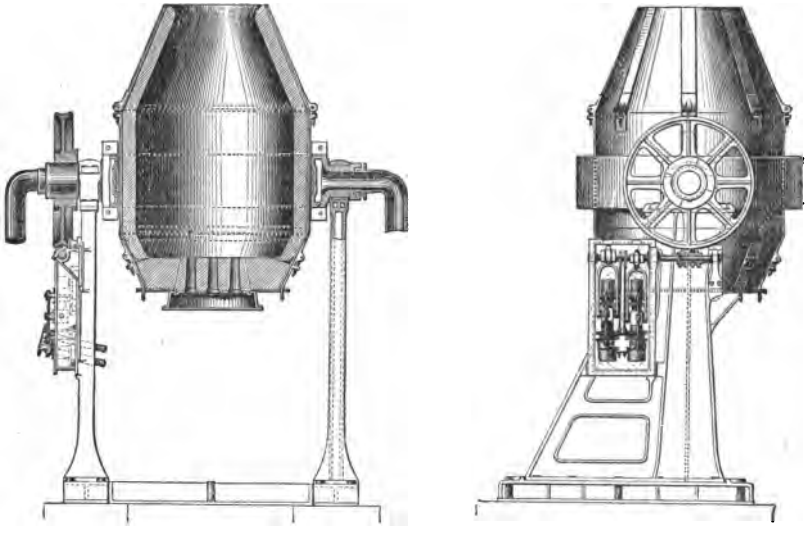
Puddled iron is a definite variety of malleable as distinct from crude iron, by reason of its structure. Having never been fused, and having been repeatedly hammered and rolled, it consists of a mass of parallel fibres arranged to form laminæ, each of which may be regarded as the representative of a member of the "pile." Between adjacent fibres and laminæ, slag, which has escaped expression, exists and renders the metal non-homogeneous. Malleable iron which has been produced by methods involving perfect fusion, and is, therefore, homogeneous and free from slag, is now largely made by processes originally devised for the production of steel. Such "ingot iron," commercially known as "mild steel," is produced by the decarburation of cast iron by the open hearth and Bessemer processes now about to be described.

2. **Purification of Iron by Methods Involving Complete Fusion of the Product.**—These methods, which have been adopted within the last thirty years, are typified by the **Bessemer process** and the **Siemens-Martin process.**

The Bessemer process consists in blowing air through fused pig iron whereby the impurities present are successively oxidised and an approximately pure iron results, to which carbon is restored (in quantity depending upon whether an ingot iron or a steel is required), by the addition of a material rich in carbon —*e.g.*, spiegel-eisen.

The operation is conducted in a "converter," shown in Fig. 15. This consists of a shell of steel plates with a refractory lining and carried by trunnions on which it can be rotated for filling and emptying. An air blast is supplied through pipes (which pass through the trunnions), whence it travels to the air box at the bottom of the converter, and thence by twyers to the interior. The usual size takes a charge of about 10 tons. As originally devised, the Bessemer converter was lined with **ganister,** a highly siliceous material, refractory at high temperatures. The acid character of this lining did not allow of the employment of iron from phosphoric ores, as the elimination of phosphorus only takes

place freely in the presence of a base capable of forming a stable phosphate with the oxidised phosphorus. Pure hæmatite pig has, therefore, to be used in an acid-lined converter. Such pig,



A. B.

Fig. 15.—Walker's 10-ton converter.
A, Vertical section. B, Side elevation.

and the iron produced from it, have the following compositions :—

	1. Bessemer pig.	2. Metal at end of blow.	3. After addition of spiegel.
	Per cent.	Per cent.	Per cent.
Carbon, ...	3·57	0·19	0·37
Silicon, ...	2·26	Trace	Trace
Manganese, ...	0·04	Trace	0·54
Sulphur, ...	0·10	0·10	0·09
Phosphorus, ...	0·07	0·07	0·05

According to the best practice, uniformity of raw material is secured by mixing the product of several blast furnaces—thus avoiding the effect of individul irregularities of working—and running the still liquid metal into a ladle, whence it is transferred to the converter. An extension of this principle has been

adopted by J. Massenez, who combines the process of mixing with a method of **desulphurisation,** the two operations being carried out by the plant shown diagrammatically in Fig. 16. The cast iron is tapped from the furnace into a ladle which is run by a locomotive to the mixer shown in the middle of the figure, and is then treated with sufficient ferro-manganese to remove the bulk of the sulphur as MnS, which floats to the top. The desulphurised iron is turned into a second ladle, shown on the right-hand side of the figure, and is conveyed to the converter (*q.v.*).

The converter is previously heated by a charge of burning coke which is raked out before the vessel is filled. The blast is started, and the converter, which was turned over to receive the charge, is raised to a vertical position. The silicon and manganese in the iron are first oxidised and the temperature considerably raised

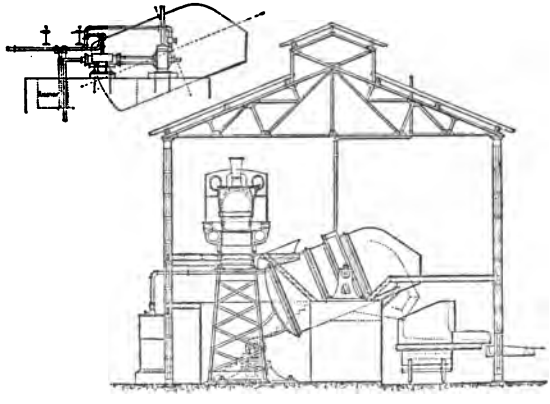


Fig. 16.—Mixer and desulphuriser.

by their heat of combustion. A slag of manganous and ferrous silicates is thus formed. In consequence of the products of combustion being solid, but little flame is visible at the mouth of the converter at this stage of the process, which lasts for some six minutes. As the silicon is removed, the graphitic carbon becomes converted into combined carbon and then burns, the charge boiling from the escape of CO, which burns at the mouth of the converter, accompanied by a shower of particles of burning iron. The silicon is a more important source of heat than is the carbon, on account of its high heat of combination with oxygen. This second stage occupies another six minutes. During a third period of six minutes the flame dies down, and is succeeded by a stream of white-hot nitrogen from the air of the blast, the oxygen of which is retained by the charge. The metal now contains mere traces of impurities (see table above), but is

slightly oxidised. The converter is inclined, and a charge of spiegel-eisen added, the amount being dependent on the grade of the required product. The contents of the converter are finally emptied into the ladle, whence, after its temperature has fallen sufficiently so that it pours quietly and is capable of yielding a sound casting, the metal is allowed to flow into vertical cast-iron ingot moulds. The effect of the spiegel-eisen is shown in column 3 in the above table. When a metal very low in carbon—*e.g.*, 0·25 per cent. is required, ferro-manganese is substituted for the spiegel-eisen, as by this means for a given content of manganese a smaller proportion of carbon is introduced. It is not found advisable to dispense with the use of spiegel-eisen or of ferro-manganese by stopping the blow when the metal contains a residual amount of carbon identical with that required in the finished product, as it is less easy to hit the precise point than to almost completely decarburise the metal, and then restore* carbon to it in known amount. Moreover, it is probable that manganese has a beneficial effect as a de-oxidant.

The need for utilising phosphoric pig has led to the use of a basic instead of an acid lining.

Thus, in the Thomas-Gilchrist process, the converters are lined with dolomite, which is either made into bricks or mixed with tar and rammed in *in situ*. The iron should be fairly rich in phosphorus, that element contributing largely to the heat generated in the blow. The charging and blowing are conducted as in the acid process, save that before charging about 10 to 15 per cent. of quicklime, calculated on the weight of the charge, is introduced, and the blow is continued past the point at which the consumption of the carbon is complete, this second period being known as the "after-blow"; during this time the phosphorus, which is the last impurity to be burnt, is oxidised and combines with the lime to form the basic slag, which is used as a fertiliser (see *Manures*, Vol. II.), or for producing phosphoric pig in the blast furnace. The production of pig rich in phosphorus is necessary, as iron poor in phosphorus, though still containing too much to be dealt with by the acid process, cannot be treated in the converter as satisfactorily as can that rich in this element. The basic slag is poured off and spiegel-eisen introduced, followed by ferro-manganese, which is added to the metal in the ladle. The following analyses illustrate the changes which occur in the composition of the metal:—

* Carbon as such has been proposed as a substitute for ferro-manganese or *spiegel-eisen*.

	1. Basic pig.	2. Metal at end of after-blow.	3. Finished metal.
	Per cent.	Per cent.	Per cent.
Carbon, ...	3·57	Trace	0·12
Silicon, ...	1·70	...	0·03
Phosphorus, ...	1·57	0·08	0·02
Manganese, ...	0·71	Trace	0·27
Sulphur, ...	0·06	0·05	0·04

The Siemens-Martin or Open Hearth Process.—The production of refined iron from crude iron can be effected in "open" hearths heated by regenerative gas furnaces (see Fig. 8, p. 67), as well as in converters. There are two forms of this process, the Siemens-Martin, in which a mixture of pig iron and scrap wrought iron is used, and the Siemens, in which pig iron and iron oxide (pure ore) are employed. In the first case the reduction of the content of pig iron in carbon and other impurities is effected (*a*) by dilution with the less impure scrap,* and (*b*) by the selective oxidation of the fused metal by the furnace gases. In the second, the oxidation of the carbon, &c., of the pig is performed by the oxygen of the ore as well as by the furnace gases. The saucer-shaped hearth of the furnace, A, which has usually a capacity of about 10 tons, is made of iron plates (kept cool by circulation of air beneath them) and is packed with highly siliceous sand, or, in the case of the **basic open hearth process,** with dolomite or magnesite burnt and ground with tar. When the furnace is white-hot, red-hot pig iron is charged, and when this is fused, scrap iron or ore (or both) is gradually added. The proportion of pig to scrap varies according to the composition of both and of that of the metal to be produced. A usual proportion is about 1 of pig to 3 of scrap. After each addition of scrap the charge is well stirred, and when complete admixture has taken place, samples are withdrawn and tested, and pig or scrap added according to requirements. Owing to the complete control of which gas firing allows over the heating of the furnace, the exact adjustment of the composition of the bath of fused metal can be attained by repeated tests and additions of the component materials. When using a basic lining, a phosphoric pig may be worked, and lime is added to the bath. As in the basic Bessemer process, the complete removal of carbon is needed to ensure oxidation of the phosphorus. Whichever process is worked, the final adjustment of the content of carbon is effected by the addition of ferro-manganese as in the Bessemer process. The process takes about

* Which is useless until it has been remelted and recovered as massive metal.

eight to ten hours, and the loss of metal amounts to 5 to 7 per cent. Soft metal (ingot iron, "mild steel") is largely made by the Siemens process, and used for boiler and ship plates, bridge work, &c., while a harder grade, which may be reckoned as a true steel, is made for railway carriage wheel tyres. The following analyses show two grades commonly made :—

	Ingot Iron.	Tyre Steel.
	Per cent.	Per cent.
Carbon, ...	0·17	0·58
Silicon, ...	0·02	0·23
Manganese, ...	0·04	0·64
Phosphorus, ...	0·06	0·03
Sulphur, ...	0·01	0·03

It has been proposed to purify crude iron by electrolysis, in a manner similar to that in use for copper, but the method has not hitherto proved practicable.

PRODUCTION OF CEMENT STEEL.—For the production of the best classes of steel—*e.g.*, tool steel—none of the foregoing processes for making ingot iron or steel of moderate hardness is well adapted, on account of the impurities—*e.g.*, S and P—which the metal retains. Steel which is to be hardened for cutting purposes contains from 0·8 to 1·5 per cent. of C, and must be as nearly as possible free from other foreign constituents. In consequence, the very purest puddled bar is taken as the raw material and carburised, and thus converted into steel, by the **cementation process.** The bars of iron, which are about 3 inches wide and $\frac{3}{4}$ inch thick, and 8 to 10 feet long, are packed in firebrick boxes, set over a long grate, in furnaces commonly heated by solid fuel. The bars are packed in these chests in alternate layers with charcoal which has passed through a $\frac{1}{2}$- to $\frac{3}{4}$-inch mesh sieve. Each chest is about 3 feet in depth, and takes a charge of 7 to 8 tons of iron. A thick layer of charcoal is placed on the top and covered with grinders' waste (siliceous and steely particles). The temperature of the furnace is kept at a bright red heat for seven to ten days, according to the content of carbon required in the finished steel, trial bars being withdrawn from time to time, and their quality judged by their fracture, which has become crystalline and lighter in colour than that of the wrought iron used as a raw material. When pure iron is heated with carbon, the latter is gradually absorbed and penetrates the mass of iron, converting it into steel. The maximum amount that can be absorbed is 5 per cent. The mechanism of the change is not yet understood. When the bars are withdrawn they are found to be covered with blisters, which are due to the production of CO by the action of the carbon on enclosed particles of slag. The "blister steel" is irregular in texture, the content of carbon decreasing from

the outside to the inside of the bars. It may be rendered homogeneous in one of two ways. Thus, the bars may be made into a bundle and welded, the product being known as "shear steel," and if then cut up and again welded, as "double-shear" steel. The second and better way to obtain a uniform product is by actual fusion in crucibles. Steel crucibles are made of refractory fireclay and plumbago, and according to modern practice are heated in a Siemens furnace. The metal is cast into ingots, and is known as "crucible cast steel," which needs reheating and hammering before it is fit for use in tool-making. The following analysis shows the composition of a good tool steel:—

Carbon,	1·14
Silicon,	0·17
Manganese,	0·10
Sulphur,	Nil.
Phosphorus,	Nil.

MALLEABLE CAST IRON.—The process of removing carbon from cast iron at a temperature below its melting point, by heating it with a solid oxidant, may be regarded as complementary to that of imparting carbon to wrought iron in the manufacture of steel by the cementation process (*v.s.*). The process of preparing malleable cast iron was formerly thought to be an example of this reaction. In this process castings of white iron containing but little silicon and manganese are packed in firebrick boxes or in cast iron crucibles in powdered hæmatite, gradually raised to a red heat, kept at that temperature for about three days, and allowed slowly to cool. The metal is malleable so that it can be forged hot, but the decarburising is only superficial, the bulk of the carbon remaining in the graphitic state.

CASE-HARDENING.—Another instance of the transference of carbon to iron from without, in the manner occurring in the cementation process, is afforded by the operation known as case-hardening. This is best carried out by heating the iron to be case-hardened in a bed of charred organic matter—such as is nitrogenous, *e.g.*, leather, bone dust, &c., being usually adopted. By this means a layer of steel, which may be as much as $\frac{1}{16}$ inch in thickness, is formed on the outside of the article treated. A slighter steel film may be obtained by sprinkling the red-hot metal with powdered potassium ferrocyanide. Armour plates for battle ships are externally hardened in this way (Harvey's process).

EFFECT OF FOREIGN ELEMENTS UPON IRON AND STEEL.—The purest iron attainable is that prepared by electrolysis and subsequent heating *in vacuo* to expel the hydrogen, with which it is always associated by the process of deposition. The amount of hydrogen thus combined amounts to 240 to 250 times the volume of the iron, corresponding with the formula $Fe_{13}H_2$. This form of iron containing hydrogen is

hard and brittle, whence its application in facing copper plates used for electrotype printing processes ; the method of depositing steel-like iron for this purpose is known as *aciertype*. Pure iron has a specific gravity which depends on the mechanical treatment to which it has been subjected, for when stressed its specific gravity is lowered. The maximum value may be taken as about 8·0. It fuses at 1,600° C. = 2,912° F. When heated to about 1,000° C. = 1,832° F., and allowed to cool spontaneously, its temperature falls regularly until a temperature of 858° C. = 1,576° F. is reached, at which point the fall is arrested for a while, and then again occurs regularly. The ratio between the rate of fall of temperature before and after the arrest and that at the period of arrest, is about 4 : 1 ; for example, in an experiment cited by Roberts-Austen the fall of temperature per second was 2° C. = 4° F. from 1,200° C. = 2,192° F. to 858° C. = 1,576° F., and less than 0·5° C. = 1° F. from 864° C. = 1,587° F. to 852° C. = 1,566° F. It is supposed from this and from other differences exhibited in the properties of approximately pure iron, that the metal exists in two allotropic forms—(1) α-iron below 858° C. = 1,576° F., and (2) β-iron above that temperature. As will be seen below, it is considered that the latter modification occurs in hardened steel, the properties of which are ascribed to its presence.

Iron is peculiarly sensitive to the influence of impurities, which may also affect the influence of each other. The impurities most commonly present in cast iron, wrought iron, ingot iron, and steel are C, Si, S, Mn, and P. As will be seen by reference to the analyses of various grades of iron already quoted, cast iron contains each of these elements in the largest proportion, including those which have a deteriorating effect. It is on account of this that cast iron is a comparatively weak and brittle material. The weakness is largely due, in grey and mottled cast iron, to scales of graphite disseminated through the metal, thus destroying its perfect continuity. When, from the absence of silicon (*v.s.*), white cast iron is produced, it is still of low strength from the effect of the sulphur and phosphorus which it contains, although their action cannot be definitely attributed to the same cause, but rather to a more subtle influence indicated below. In the best wrought iron, ingot iron and steel, the quantities of S and P are reduced to a minimum, for when present in appreciable amount—as in the case of puddled iron —they only exist as constituents of interstitial slag.

Carbon is by far the most important of the foreign elements present in commercial iron. The graphite which occurs in grey cast iron is not found in wrought iron, ingot iron, or steel. According to Ledebur, carbon, in a state similar to but not identical with graphite, may be formed by prolonged heating of iron containing the forms of carbon next to be mentioned. On the relations of these two remaining forms of carbon (" hard-

ening carbon" and "carbide carbon") the explanation of the phenomena of hardening, tempering, and annealing largely depends. It is this capability of being hardened, tempered, and annealed which constitutes the essential difference between steel and wrought or ingot iron, and it first becomes evident when the proportion of carbon exceeds 0·25 per cent. It must be understood that this statement applies to iron containing carbon and no other impurity, as other elements—*e.g.*, phosphorus or sulphur—may exhibit analogous properties with a lower percentage of carbon. The hardening effect of these cannot be substituted for that of carbon, as the former gives "cold-short" iron—*i.e.*, a metal which is brittle (especially to shock)—and the latter "red-short" iron—viz., one which is brittle at a red heat and cannot be worked.

In the following description of the process of hardening, true steel, consisting of iron with more than 0·25 per cent. of C and a minimum quantity of other elements, will be spoken of. On heating steel above 858° C. = 1,576° F., and cooling it suddenly —*e.g.*, by plunging it into water—it will be rendered hard, whereas if allowed to cool slowly from this temperature it is comparatively soft. Such process of hardening is always adopted for steel tools—*i.e.*, those capable of taking and retaining a cutting edge. It is obvious that as the steel after hardening cannot be worked except by grinding, the tool must have received its shape before hardening, so that nothing remains but to grind it to an edge. But few tools can be used in as hard and brittle a condition as that obtained by direct quenching from a red heat in cold water. The excessive hardness must be removed by *tempering* in order that the edge of the tool may not be easily chipped but may possess a certain elasticity or springiness. The process consists in gradually reheating the hardened steel to a temperature, considerably short of redness, proper to the particular class of tool to be prepared, and quenching in water when this is reached. These temperatures are indicated by various colourations of the bright steel surface, and may be stated as follows:—

Colouration.	Temperature.	Class of Tool.
Faint yellow, . .	220° C. = 428° F.	Surgical instruments.
Straw yellow, . .	230° C. = 446° F.	Razors.
Full yellow, . .	243° C. = 469° F.	Penknives.
Brownish-yellow, .	255° C. = 491° F.	Chisels and shears.
Brown, . . .	265° C. = 509° F.	Axes and plane irons.
Purple, . . .	277° C. = 531° F.	Table knives.
Bright blue, . .	288° C. = 550° F.	Swords and springs.*

* These figures are only of limited significance because it has been found that prolonged exposure to a lower temperature will produce the same colour as will a short exposure to a higher temperature.

It is found that unless steel be heated above its critical temperature (*v.i.*) it cannot be hardened by quenching, nor is it hardened if it be cooled slowly from this temperature ("annealed"). It is obvious that inasmuch as there can be various grades of rapidity of quenching (*e.g.*, by the use of mercury, cold water, hot water, and hot oil) the hardening of steel may be more or less perfect, and it is possible, by limiting the hardening in this way, to attain a given degree of hardness or "temper" by a single operation.

When hardened steel is dissolved in dilute hydrochloric or sulphuric acid, nearly the whole of its carbon is evolved as hydrocarbons. When fully annealed, the carbon is left, on dissolution of the steel in the same acids, in a form apparently combined with iron as a carbide, corresponding with the formula Fe_3C. Hardened steel that has been "tempered" or "let down," or steel that has been imperfectly hardened contains carbon in both forms. The distinction, already mentioned, has thus arisen between hardening carbon and carbide carbon. The former appears to form with the steel a solidified solution, while the latter is diffused through the metal as grey scales, both conditions being recognisable in the fracture of the metal. Reference has already been made to the fact that when pure iron is cooled from a bright red heat it passes through a stage when its fall of temperature is arrested at 858° C. = 1,576° F. (the **critical temperature** of iron). In the case of a low carbon steel (*e.g.*, 0·25 to 0·5 per cent. C.) this arrest occurs at a lower temperature, 720° C. = 1,328° F., and is followed by a second arrest at about 657° C. = 1,215° F. The first of these is considered to be due to change of β-iron into α-iron, the second to the change of the dissolved hardening carbon into the combined carbide carbon, as is demonstrable by the behaviour of the steel on dissolution in acid, already referred to.

Since the hardening carbon is found to be retained in this condition when the steel is quenched, it is supposed that these arrests, and the changes to which they are due, do not occur during the quenching, but that the state of both iron and carbon proper to a temperature above the highest critical point (corresponding with β-iron and hardening carbon) is maintained. This view receives confirmation from the fact that in the cooling of a high carbon steel (1·25 per cent. C.) the two arrests are merged into one which is intermediate between the points already quoted (occurring at the temperature of 670° C. = 1,238° F.), and is so strongly marked as to perceptibly raise the temperature of the metal, producing the phenomenon known as **recalescence.** In this recalescence the rise of the temperature is chiefly due to the combination of dissolved (hardening) carbon with iron, yielding combined (carbide) carbon. This critical point, due mainly to the change of condition of the carbon, was one

of the early observations that led to the formulation of the above hypothesis, which is supported by the fact that steel cannot be efficiently hardened by quenching unless previously heated to above the critical point of the iron. The modern view of the nature of steel is that when soft it consists of α-iron and carbide carbon, and when hard of β-iron and hardening carbon. Further, that the hardness of hardened steel is not due to any property conferred by the carbon, but to the existence of the iron in the β state. There is, however, no direct evidence that β-iron free from carbon is hard. Thus, pure iron when heated above 858° C. = 1,576° F. and quenched, is not hardened, although it has existed in the β condition. To induce its retention in the β condition—that is, to prevent the change which is indicated by the occurrence of a point of arrest at 858° C. = 1,576° F., the presence of carbon or some element capable of the same function is necessary. Thus, iron containing small proportions of manganese shows a retardation at a point rather below the point of arrest for carbon steel, and when the quantity is increased to 7 per cent. a material (manganese steel) is obtained in which the iron appears to exist in the β condition and to be consequently hard. **Manganese steel,** which is the name applied to alloys of iron and manganese containing 7 to 12 per cent. Mn, is extremely tough and hard, on which account it has found but few applications, as it cannot be worked in the same way as hard carbon steel by annealing, machining, and rehardening. It is, however, somewhat softened by heating for two hours at 550° C. = 922° F., a fact which may aid its utilisation. It is remarkable for being quite unattracted by a magnet, although both its component metals are magnetic. The modification obtained by the annealing process just mentioned is magnetic.

The influence of nickel is somewhat similar to that of manganese on steel, in that small proportions, up to 5 per cent., increase the hardness and toughness of the product, and larger proportions, 21 per cent. and over, form with the iron an alloy of characteristic properties. Thus, nickel steel with 21 per cent. of nickel is non-magnetic at the ordinary temperature, and is therefore considered to contain iron in the β state, but it becomes magnetic on cooling strongly in a mixture of solid CO_2 and ether (−79° C. = −110° F.).

Other special steels are tungsten steel with 7 to 12 per cent. W, and chromium steel with 0·5 to 10 per cent. of chromium, both being hard and suitable for special uses, such as the manufacture of turning tools and railway wheel tyres (see p. 19).

The addition of aluminium to steel is said to improve the ingots made therefrom by increasing the fluidity of the metal and removing oxygen. Aluminium is generally added in the same manner as manganese—viz., as a ferro-alloy. Ferro-alloys, such as ferro-manganese, ferro-chromium, and ferro-silicon, used for introducing these foreign elements, are produced in the blast

furnace by the reduction of ores rich in the desired elements (*cf.* p. 135).

The grades of ordinary carbon steel most generally used, range from 0·2 per cent. C (practically an ingot iron) to 1·5 per cent. C (a razor steel). Thus, boiler plates, ship plates, and bridge members will contain 0·2 per cent.; rails, 0·35 to 0·45 per cent.; tyres and guns, about 0·5 per cent.; armour plates, 0·7 to 0·8 per cent.; projectiles, 0·8 to 1·0 per cent.; tool steel, 1 to 1·2 per cent.; razor steel, 1·5 per cent.; and draw-plate steel, 2 to 3 per cent. C. The simultaneous presence of 0·5 per cent. Mn may be taken as raising the grade of steel equivalently to an additional 0·1 per cent. C.

Apart from the effect on steel of the condition of the iron and of the carbon, is the influence of the actual crystalline structure of the metal. Other things being equal, a steel with a coarse crystalline structure is weaker than a steel with a fine structure. Overheating steel, or heating it considerably above its critical point, causes it to assume a coarse structure whatever the rate of cooling. This crystalline structure can be broken down by forging the hot steel, a plan adopted for heavy guns.

The mechanical effect of hardening steel is shown (1) by its change in specific gravity—*e.g.*, 7·9 before hardening, and 7·6 afterwards—the dilatation being about 5 per cent.; (2) by its increase in tensile strength—*e.g.*, for a steel containing 0·8 per cent. C, 64 tons per square inch when hardened, in place of 44 tons when unhardened; (3) decrease of ductility—for the same steel, an extension of 8 per cent. of its length when unhardened, and 1 per cent. when hardened. The same effect on tensile strength and ductility that is produced by hardening (quenching) can be obtained by subjecting the metal to severe mechanical stress, such as occurs in wire drawing. Steel wire, although not hardened by quenching, may have a tensile strength exceeding that of steel of the same grade that has been purposely hardened. This hardness, like that due to quenching, is removed by annealing.

The influence of impurities on steel has been referred to the relation between the atomic volume of iron and that of its associated elements. The following table shows that the ordinary impurities may be divided into two groups, according as their atomic volume is below or above that of iron (7·2):—

	I. Atomic Volume.		II. Atomic Volume.
C, ...	3·6	Cr, ...	7·7
B, ...	4·1	W, ...	9·6
Ni, ...	6·7	Si, ...	11·2
Mn, ...	6·9	As, ...	13·2
Cu, ...	7·1	P, ...	13·5
		S, ...	15·7

The elements in the first series are believed to favour the retention of iron in the β state, and tend to the production of a hard metal; those in the second series are supposed to hinder the formation of β iron, and yield a softer, more ductile material. This view is not strictly in accord with the known influence of several of the elements in series II., notably S and P (*v.s.*).

COPPER.

The following are the chief sources of copper:—**Native Copper.**—Considerable masses of metallic copper occur native in the neighbourhood of Lake Superior. In other districts—*e.g.*, in Cornwall—it is found in veins distributed, in crystalline form, through granites and other rocks. Copper sand containing 60 to 80 per cent. of copper, the balance being quartz, is found in Chili, and is known as "copper barilla." It constitutes a minor source of copper.

Red Copper Ore.—Pure specimens of this mineral **(cuprite)** have the composition Cu_2O. It is found in Cornwall, but the quantity is small compared with that of the sulphide ores. Black oxide of copper (CuO) is also found in slight amount.

Carbonates of Copper, containing various proportions of copper hydroxide and copper carbonate, are found as **malachite,** $CuCO_3.Cu(OH)_2$, and **blue malachite** or **azurite,** $2CuCO_3.Cu(OH)_2$. The most noteworthy deposits of these minerals are those at Burra-Burra in Australia.

Copper Pyrites.—This is one of the most abundant of copper ores. Pure specimens have the composition $Cu_2S.Fe_2S_3$, but the ores which are worked contain a certain amount of gangue and generally an excess of sulphide of iron, and are frequently associated with arsenic. Indeed, iron pyrites containing copper (see *Manufacture of Vitriol*, Vol. II.), is worked for the copper which it contains.

A variety richer in cuprous sulphide than is ordinary copper pyrites, corresponding with the formula $3Cu_2S.Fe_2S_3$, is known as **peacock copper** from its variegated colours.

Copper Glance.—This ore corresponds with the formula Cu_2S (cuprous sulphide). It is found in Cornwall, and occurs in Siberia, Saxony, and elsewhere.

Grey Copper Ore consists of copper sulphide associated with antimony sulphide, its composition being very various.

Cupriferous Schists, consisting of bituminous shale through which copper pyrites and copper glance are disseminated, occur at Mansfeld.

WINNING OF COPPER FROM ITS ORES.

A. **DRY PROCESSES.**—The following general principles may be said to control the dry processes for the extraction of

copper :—The production of copper from its ores differs essentially from that of iron by reason of the fact that the chief ores worked contain copper as sulphide instead of as oxide, and that sulphur, instead of oxygen, is, therefore, the element to be removed. Seeing that sulphur, unlike oxygen, cannot be removed by reduction with carbon, the formation of CS_2 being endothermic, it must first be eliminated as SO_2 by an oxidising process, the copper being converted into oxide.

If pure copper sulphides were being worked, reduction of the oxide to metal by carbon could be effected at this stage,* just as iron ores are reduced in a blast furnace; but, owing to the fact that iron is a constant constituent, the roasted ore would contain oxides of iron; these would also be reduced, yielding a mass which would prove unmanageable, on account of the infusibility of the iron. It thus happens that in any process for smelting copper from an ore containing copper and iron, the iron must be eliminated before the copper can be obtained as metal. In order to effect this, advantage is taken of the greater stability of copper sulphide than that of iron sulphide in an oxidising atmosphere.

When a mixture of the sulphides of iron and copper is roasted, the greater part of the iron is converted into oxide, while the bulk of the copper remains as sulphide. Even should these reactions be incomplete, in the sense that a portion of the iron remains as sulphide, while a portion of the copper is converted into oxide, all the copper may be ultimately obtained as sulphide on account of the ease with which oxide of iron and sulphide of copper interact. When all the copper has been obtained as sulphide and all the iron as oxide, the latter can be removed by suitable fluxes.

Approximately pure sulphide of copper having been thus obtained, it is only necessary to replace a portion of its sulphur by oxygen, and to subsequently cause the oxide of copper to react with the residual sulphide, thus :—

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

Crude copper differs from most other crude metals, in respect of the fact that it can be economically refined by electrolysis (*v.i.*), as well as by ordinary dry methods.

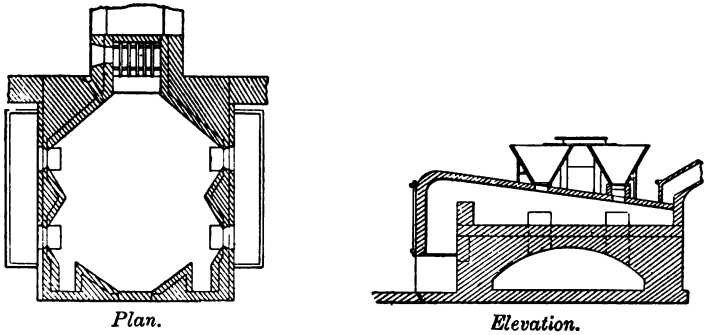
Although the processes for smelting copper are numerous and complicated, they all depend upon the general principles expounded in the foregoing paragraphs. The description of the **Welsh smelting method** will serve as one of a type to which others are referable. In this process the following operations are usually carried out :—

1. **Calcination.**—The object of this depends largely on the

* Actually, pure copper sulphide is capable of "self-reduction" (p. 124), thus :—$Cu_2S + 2CuO = 4Cu + SO_2$, so that complete roasting and reduction with carbon is unnecessary; it is, nevertheless, practised in typical German processes—*e.g.*, that which is known as the Mansfeld process (*v.i.*).

nature of the ore. In the case of copper pyrites, partial oxidation of the iron and sulphur and elimination of arsenic and antimony, are the chief ends to be attained.

In the Welsh process this is generally effected in a reverberatory furnace, with a grate small in comparison with the hearth, so that the temperature is low enough for efficient calcination. A furnace of this type is shown in Fig. 17. The main reaction is the removal of about half the sulphur as SO_2, and the greater part of the arsenic as As_4O_6. Antimony is also partly eliminated. The resulting fumes, "copper smoke," will contain, besides the above constituents, SO_3 evolved from ferrous sulphate, into which a portion of the iron sulphide has been oxidised, and HF from the interaction of the SO_3 with fluor spar (CaF_2) present in the gangue. These fumes are condensed as much as possible, and the arsenic recovered. The calcined ore consists essentially of copper as sulphide with some oxide; iron as oxide with some



Plan. *Elevation.*

Fig. 17.—Reverberatory roasting furnace.

sulphide; a portion of the arsenic and antimony as arseniate and antimoniate; and unchanged gangue. When the SO_2 is to be used for vitriol making, calcination is performed in roasters, from which the fire gases are excluded (*e.g.*, muffles), and from which the SO_2 can be drawn off in a fairly concentrated form. Calcination can also be performed by roasting the ore in heaps, constructed essentially in the manner of a charcoal heap; a portion of the sulphur distils off and may be collected in hollows left in the heap. When poor ores are thus treated it is found that the centre of each lump has become richer in copper than its outer portion; a concentration is thus effected by this process, which is known as "kernel-roasting." The substitution of stalls (*cf. Coke Manufacture*, Vol. II.), for heaps is practised when the utilisation of SO_2 is required; the gas is drawn off through flues in the walls of the stalls. Narrow vertical kilns, with horizontal bars (*Gerstenhöfer* kilns) down which the ore is caused to pass,

meeting a current of hot air on its way, are also employed when calcination with the recovery of SO_2 is desired.

2. **Fusion for Coarse Metal.**—In this operation the bulk of the iron is to be removed as silicate. For this purpose it

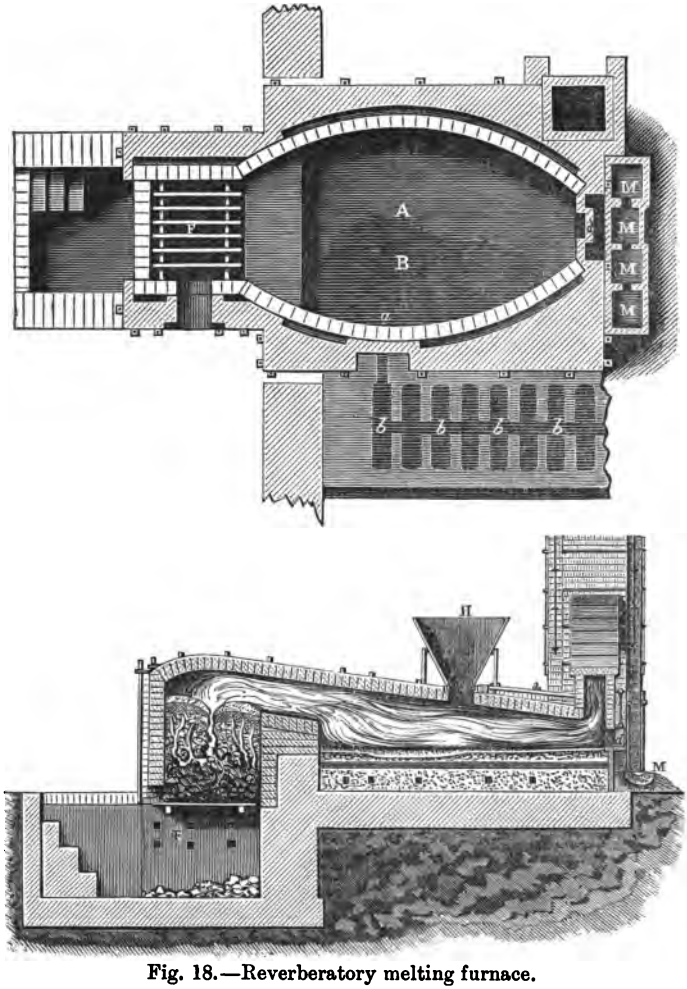


Fig. 18.—Reverberatory melting furnace.
A, Hearth; B, hollow in sand; H, hopper; *d*, door; M M, moulds; *a*, tamping hole; *b*, ingot moulds.

must all be present as a base (viz., as its oxide), and the residual iron sulphide, left by calcination, must, therefore, be converted into oxide. As has been already mentioned, this is to some

extent effected by the interaction of the copper oxide, obtained in calcination, with the iron sulphide; but, as an auxiliary, copper ores in which the copper is present as oxide are added.* The siliceous flux for the removal of the iron is provided partly by the gangue and partly by the slag from a succeeding operation, this slag, inasmuch as it contains about 4 per cent. of copper, being too valuable to throw away. The furnace in which the fusion for coarse metal is conducted is of the reverberatory type (see Fig. 18).

Its hearth, A, is lined with sand and is small relatively to the grate, since a high temperature is required. A depression in the sand hearth at B serves as a collecting well for the fused matte. The mixture of calcined sulphide ore and raw oxide ore (about 2 : 1) is introduced into the furnace through the hopper, H, and the slag from a succeeding operation (thus worked up for its copper) is thrown in through the door, *d*. The furnace is then closed and the charge brought to fusion, in which condition it is maintained for six to seven hours. The slag is then raked out through the door, *d*, into the moulds, M M.

The matte is drawn off through the tamping hole, *a*, into the ingot moulds, *b*. The slag, known as **ore furnace slag**, consists essentially of ferrous silicate, and should not contain much above 0·25 per cent. of copper; it is then regarded as "clean" and rejected. It is found difficult to obtain clean slags when working with raw material containing more than 15 per cent. of copper, and when the content falls below 9 per cent. the cost of heating the gangue becomes unduly great. The matte or "coarse metal" contains from 35 to 39 per cent. of copper, and has a similar composition to that of pure copper pyrites, the proportion of iron and sulphur having been reduced (see table, p. 162).

3. **Calcination of Coarse Metal.**—The granulated or crushed matte is calcined in a reverberatory furnace with a large hearth. The effect of this roasting is to substitute oxygen for a portion of the sulphur, the main oxidation again taking effect on the iron sulphide, as in the original calcination of the sulphide ore. Calcination is sometimes carried out in a Gerstenhöfer kiln, such as has been described on p. 155, so that SO_2 can be collected and used.

4. **Fusion for Fine Metal.**—The calcined coarse metal is fused in a reverberatory furnace—which has a depression in the bed, and is in all respects similar to that used in the fusion for coarse metal — with oxidised ores and sometimes with crude copper precipitate from wet processes of extraction, and with rich slags from succeeding operations. The added oxidised ore may amount to as much as half the weight of the calcined coarse metal. The mixture is so proportioned that there shall

* In the event of over-calcination, instead of under-calcination having taken place, the composition of the charge is corrected by the addition of sulphide ores instead of oxide ores.

be sufficient oxide of copper to react with the remaining ferrous sulphide,* and enough siliceous matter to flux the oxide of iron produced; the resulting matte consists essentially of cuprous sulphide, "white metal," containing about 70 per cent. Cu. Should the iron sulphide have been incompletely oxidised, "blue metal" containing 50 to 55 per cent. Cu is obtained, and in the event of the oxidation by means of the added ores having been pushed further than usual, self-reduction will occur and "pimple metal," containing about 76 per cent. Cu, will be produced. Pimple metal owes its name to its roughened surface, due to the escape of SO_2 from the metal as it solidifies. A portion of the copper is present in the metallic state, frequently having a fibrous mossy appearance (*moss copper*). The copper thus separated acts as a solvent for a large portion of such impurities as have persisted up to the present stage—*e.g.*, As and Sb—and settles to the bottom of the ingots into which the matte is cast; the upper and purer portions of the ingots are used for the "best selecting process" subsequently described, the lower portions going to the roaster (*v.i.*). The slags from the white metal consist of ferrous silicate, but inasmuch as the charge is rich in copper oxide, some copper silicate passes into the slag (**metal slag** containing about 4 per cent. of copper). To recover this copper the slag is returned to the furnace for fusion for coarse metal, already described.

5. **Roasting and Self-Reduction.**—In order that self-reduction may be brought about, it is necessary to roast a portion of the matte to oxide so that it may react upon the remaining cuprous sulphide and form metallic copper and SO_2, according to the equation given above. The ingots of fine metal are placed on the hearth of a reverberatory furnace—similar to that used in the preceding process, but provided with a greater number of air inlets—and slowly melted down, free access of air being allowed and the slag being frequently skimmed off. The molten mass soon begins to boil with the escape of SO_2. The air ways are closed, the slag skimmed off the surface, and the "blister copper" run into ingots. The escape of gas from the molten metal renders it vesicular and blistered on the surface. It contains about 98 per cent. Cu. The slags (**roaster slags**) result from the combination of the oxides of copper and iron with the silica of the furnace bed, and contain about 10 per cent. of Cu. They are worked up in the fusion for fine metal.

It will be seen that the processes hitherto described consist of oxidations alternated with reactions between oxides and sulphides, a crude copper being thus obtained. In order to effect the separation of the products of the reaction between

* A further adjustment of the proportion may be requisite if it has been disturbed by the introduction of crude copper precipitate, which may be provided with the necessary sulphur by the addition of sulphide ores.

sulphides and oxides, in the form of a matte, a fusion is necessary, any remaining oxides being removed as slag. In all cases three pairs of these two types of process—roasting for oxidation and fusion for reaction—are necessary, the last pair (*v.s.* subsection 5) being performed in the same furnace, and thus appearing as a single operation. When the fourth operation (fusion for fine metal) has failed to produce a matte sufficiently pure for the final roasting, another pair of operations must be carried out in order to bring the copper up to a grade suitable for refining. The product of this extra inserted pair of operations is known as "coarse" or "black copper," and contains about 80 per cent. of Cu. It is roasted to blister copper as already described.

6. **Refining.**—The crude blister copper usually contains S, As, Sb, Sn, Pb, Bi, Fe, Ni, Ag and Au. Of these, sulphur is the chief impurity, though copper from arsenical ores may retain several per cent. of arsenic. The refining process consists essentially of regulated and limited oxidation. The blister copper is piled on the hearth of the refinery, which is an ordinary roasting furnace with an inclined hearth, and slowly fused in an oxidising atmosphere. The charge is rabbled and skimmed at intervals until it has arrived at the stage of "dry copper," so called from the dull red colour of a fractured surface. This condition is due to the presence of cuprous oxide dissolved in the copper, and is an indication that the impurities have been oxidised. It is considered that the process of oxidation is much promoted by the conveyance of oxygen in the form of cuprous oxide to the interior of the mass of fused copper on the refinery hearth. A similar but more efficient agent is sometimes used—viz., oxide of lead (produced by the addition of metallic lead to the charge), which is more easily reducible by the impurities to be oxidised than is cuprous oxide; this method of treatment is termed "scorification." The slag (**refinery slag**) contains the above-mentioned impurities as oxides—except that some of the sulphur and arsenic has been volatilised—and silica from the furnace lining. It also contains much copper oxide (corresponding with a content of about 55 per cent. Cu in the slag), to recover which the slag is reworked in the fusion for fine metal.

Dry copper containing cuprous oxide is useless for most purposes, being brittle ("short"); accordingly, as soon as the slag is removed, the surface of the metal is covered with anthracite or charcoal, and after a short time a pole of green wood is worked in the charge. The gases thereby evolved from the wood effect the reduction of the cuprous oxide and toughen the metal, converting it into "tough-pitch copper." It is found advantageous not to push the *poling* too far, as a small quantity of cuprous oxide improves the quality of ordinary copper (see *Influence of Impurities on Copper*, below). The tough copper is ladled into ingots. The substitution of other reducing agents for the carbon

of the poling has been attempted, the greatest success having attended the use of phosphorus, in the form of copper containing 7 per cent. of this element. Only traces of phosphorus remain in the finished copper. Aluminium and zinc will effect a similar reduction.

The removal of arsenic from arsenical blister copper and arsenical copper bottoms (*v.i.*) is advantageously effected by refining in a furnace with a basic-lined hearth, such as is used in steel-making, because impurities yielding acid oxides — *e.g.*, arsenic and antimony — are thus more easily eliminated.

Process of making "Best Selected" Copper.—It has already been indicated that when oxidation occurs, in the process of fusion for fine or white metal, beyond the point at which all the iron is converted into oxide, a portion of the copper appears as metal, and this dissolves a large proportion of the impurities of the matte. It is found advantageous to exaggerate this effect, and to thus obtain a matte which can be more efficiently refined than can ordinary fine metal. When this method is adopted, the process is conducted in a separate furnace, in which the fine metal, instead of being made to undergo complete self-reduction, as in the roaster furnace (*v.s.* sub-section 5), is melted down, and is tapped when about one-fourth of the copper has been reduced. When the matte is cast into ingots, the metal settles to the bottom, and is afterwards broken off. The refined matte ("close regulus," containing 79 per cent. of Cu) is almost pure

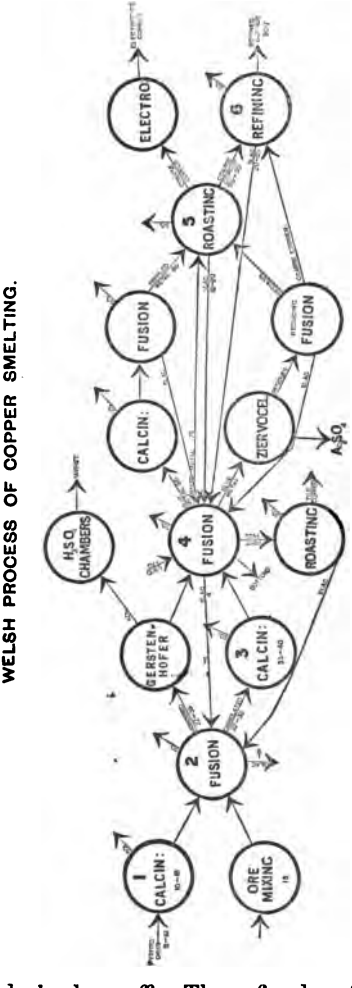


Fig. 19.

Cu_2S (which contains 80 per cent. of Cu), and is put through the roasting and refining process already described (Nos. 5 and 6). The copper thus obtained is "best selected." The lower portions of the ingots are known as "bottoms," and are rich in the impurities (notably arsenic) present in the original fine metal. They are refined in the same manner as is blister copper, preferably on a basic hearth, and yield a copper of a grade lower than best selected.

The diagram on the preceding page (Fig. 19) gives a graphic representation of the stages of the Welsh process of copper smelting.

The gradual change in chemical composition of the products of copper smelting by the Welsh process, from the ore to tough pitch copper, is shown in the accompanying table of analyses :—

	Ore.	Roasted Ore.	Coarse Metal.	Roasted Coarse Metal.	Fine Metal.
Copper, .	12	13	34	37	72
Iron, . .	26	28	35	38	6
Sulphur, .	30	21	30	15	22
Gangue, .	32	34	1	1	...
Oxygen, .	...	4	...	9	...
	100	100	100	100	100

	Bottoms.*	Blister Copper.	Refined Copper.	Tough Pitch Copper.	Best Selected.
Copper, . .	92·32	98·46	98·90	99·61	99·89
Sulphur, . .	0·95	trace	trace	trace	...
Lead, . .	0·92	0·02	0·02	0·02	trace
Bismuth, . .	0·06	0·04	...	...	0·02
Arsenic, . .	5·09	0·84	0·02	0·02	0·05
Antimony, .	0·27	trace	trace	trace	trace
Phosphorus, .	0·05	0·01	...	...	...
Iron, . .	0·02	0·02	trace	trace	trace
Nickel and cobalt,	0·12	trace	0·22	0·21	trace
Silver, . .	0·02	0·02	0·03	0·03	...
Oxygen, . .	...	...	0·75	0·08	...
	99·82	99·41	99·94	99·97	99·96

The products obtained in copper smelting and refining necessarily vary according to the nature of the raw material and the mode of working; the figures given above are, therefore, to be taken as representative examples and not as rigid standards.

Typical German Process of Copper Smelting.—This differs from the Welsh process already dealt with, in that kilns

* *Journ. Soc. Chem. Ind.*, 1891, p. 4.

and blast furnaces are respectively substituted for the calcination furnaces and fusion furnaces described above. Moreover, the fine metal is roasted "dead"—*i.e.*, converted into cupric oxide —and reduced by carbon in a reverberatory furnace, this pair of operations taking the place of the self-reduction of the Welsh process. For most ores the Welsh is now largely substituted for the German typical method, as although it needs more fuel it avoids the strong reducing action of the blast furnace which tends to yield an impure metal.

The Mansfeld Process of Winning Copper (and Silver). —This process is particularly adapted for ores poor in copper, but containing sufficient silver to pay for recovery. This is especially the case with the Mansfeld cupriferous schists. A typical ore of this class has the following composition :—

	Per cent.
SiO_2,	32·78
Al_2O_3,	11·28
CaO,	14·31
MgO,	4·53
CO_2,	13·51
Fe,	0·85
Cu,	2·93
Ag,	0·01
S,	3·96
Bituminous matter, &c.,	14·07

The ore is burnt in heaps; the bitumen and some of the sulphur are eliminated, but care is taken to retain the copper as sulphide. It is then fused in blast furnaces with slags from a succeeding operation and fluor spar. The resulting coarse metal contains from 30 to 45 per cent. of copper, and is roasted in kilns, for which purpose it is mixed with 85 per cent. of already roasted coarse metal to avoid fusion. The fusion for fine metal (*spurstein*) is conducted in a reverberatory furnace. As it is important that "moss copper" (*v.s.*) should not separate, some unroasted coarse metal is added to the charge to keep the copper as sulphide. The fine metal contains 74 to 75 per cent. of Cu and 0·3 per cent. of Ag. The next process has for its object the complete oxidation of the copper, and, concomitantly, the conversion of silver into sulphate. This is carried out (in Ziervogel's process) by roasting the ground fine metal in a reverberatory furnace, and can only be effected by due attention to the conditions of oxidation; these will be dealt with more particularly under *Silver*. The silver sulphate is leached out, precipitated by copper and worked up. The residual copper oxide is dried, mixed with small coal, reduced in a reverberatory furnace, and refined in the usual way.

The Use of the Bessemer Converter in Winning Copper. —The advantage gained by the use of the converter in refining iron chiefly consists in the circumstance that the impurities, in

the process of removal by oxidation, themselves furnish the heat necessary to carry on the operation and keep the metal thoroughly liquid. In the case of iron, the chief impurities, carbon, silicon and manganese, evolve much heat on oxidation, and thereby actually raise the temperature of the charge in spite of losses of heat by radiation and other causes. With copper, on the contrary, the chief impurities, sulphur, iron and arsenic, have comparatively low heats of combination with oxygen, and are also usually smaller in quantity than the impurities in iron. It follows that although the specific heat of copper (0·095) and its melting point (1,000° C. = 1,832° F.) are lower than the same constants for iron (0·112 and 1,400° C. = 2,552° F.), the heat evolved in bessemerising crude copper (*e.g.*, blister copper) is insufficient to maintain the metal in a molten condition. The attempt to refine crude copper by ordinary bessemerising has, therefore, been abandoned, and the old refining process, costly in fuel and labour, retained of necessity. By starting with a cruder product than blister copper, and thus increasing the quantity of combustible material, it is possible, however, to evolve sufficient heat to maintain the charge in a liquid condi-

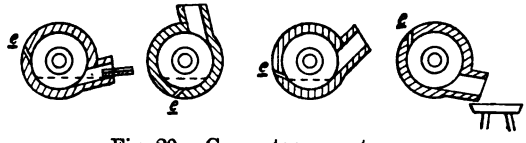


Fig. 20.—Converter—*e*, a twyer.

tion, and to oxidise it until the bulk of the sulphur and iron is eliminated and a grade of crude copper corresponding with the blister copper of the Welsh process obtained.

The **Manhés process** is based on this principle. A matte corresponding with blue metal—*i.e.*, of a composition between that of coarse metal and fine metal (*v.s.*)—is produced, run into a converter, and oxidised by a blast directed at first from below the charge and afterwards from twyers from the side of the converter, so that as the copper is reduced to metal and sinks to the bottom of the charge, it may cease to be acted on by the blast, which is directed upon the still unoxidised and specifically lighter matte.

A recent form of converter consists of a cylindrical vessel with its longer axis horizontal and provided with an inlet and outlet at its ends, so that the flame of a furnace can be turned through it in order to melt the charge within it before bessemerising. The twyers are placed in a row along the side of the cylinder, and are so connected with the pipe conveying the blast that by a partial rotation of the cylinder the air may be either forced through the molten charge at any desired depth, or directed down upon its surface without breaking joint with the air

supply. A cross-section of the cylinder in different positions is shown in Fig. 20, *e* representing one of the twyers. The attachment of a jointed tube capable of flexure to *e* for the conveyance of the blast will be readily appreciated. The copper obtained has a composition averaging Cu 98·7, S 0·85, Fe 0·45 per cent.

WET PROCESSES OF COPPER EXTRACTION. — When ores containing copper sulphide are exposed to air in a moist condition, the sulphide is oxidised to sulphate and may be leached out with water. The methods depending on the application of this, and like principles, are available for ores containing about 3 per cent. Cu, which are too poor to smelt profitably. In certain copper-bearing strata this extraction takes place naturally, yielding a solution of copper sulphate, the "blue-water" of some copper mines. The same process is put in use artificially by spreading the ore in heaps, provided with trenches to act as drains, and frequently watering it during many months. Owing to the slow oxidation of large masses of ore in this way, a considerable quantity of heat is generated; the temperature is best kept as 38° C. = 100° F. by regulating the water supply, for the production of steam would exclude air. On the other hand, too low a temperature unduly retards the process. The oxidation proceeds mainly at the expense of the copper sulphide, and when this is nearly exhausted (*e.g.*, to 0·25 per cent. Cu) the ore is still serviceable as a sulphur ore (for vitriol making). The solution of copper sulphate, whether obtained naturally or artificially, is run into asphalted tanks filled with iron pigs, by means of which the copper is precipitated; the crude product (containing 65 per cent. of Cu, the balance being chiefly graphite and rust) is sent into the market as "cement copper." The presence of much ferric sulphate (from the iron sulphide of the ore) in the liquors, frequently causes the consumption of three times as much iron as is necessary to precipitate the copper, the difference being due to the reduction of ferric to ferrous sulphate. It is advantageous, as far as economy of pig or scrap iron is concerned, to roast the ore before extraction, as the amount of ferric sulphate in the liquor is thus decreased and the amount of pig iron consumed by it correspondingly diminished.

Large quantities of pyrites containing about 3 per cent. Cu are burnt for vitriol making, and the residue (chiefly ferric oxide) worked up for copper. This is generally done by grinding the spent pyrites with common salt and calcining the mixture in a muffle furnace. The sulphur left in the ore by the vitriol maker is oxidised, copper sulphate being formed. This reacts with the salt, yielding cupric chloride and sodium sulphate. The "chlorinated" ore is leached out with the liquors (containing HCl) that have been condensed in the towers attached to the furnace flues, and the copper is precipitated by iron in

the usual way. The spent ore, "purple ore," is used for the fettling of puddling furnaces. A similar chlorinating roasting is carried out in heaps at the mines when the sulphur is not utilised.

Another method of dissolving copper from its sulphide ores depends on the fact that when a cupriferous pyrites is treated with a solution of a ferric salt—*e.g.*, Fe_2Cl_6—the cuprous sulphide reduces the ferric chloride with the formation of cuprous chloride and free sulphur,

$$Cu_2S + Fe_2Cl_6 = 2FeCl_2 + Cu_2Cl_2 + S.$$

A portion of the cuprous chloride is oxidised by the air to cupric chloride. In practice, ferric chloride is not used, but a mixture of ferric sulphate and salt (potentially ferric chloride), such as results by adding salt to liquors from the precipitating tanks, or by leaching the chlorinated ore that has been roasted in heaps in the manner described in the preceding paragraph. The excess of salt serves to dissolve the cuprous chloride. The precipitation of the copper is effected as usual.

THE ELECTROLYTIC WINNING AND REFINING OF COPPER.—As stated above, cement copper is a crude product containing 60 to 80 per cent. Cu, the remainder being impurities (graphite and rust) from the iron. By using electrical energy instead of the chemical energy of iron to reduce the copper, a pure metal can be obtained at a single operation; this is rendered possible because of the greater ease with which copper is deposited from an acid solution than is the chief impurity present—viz., iron—a fact which is borne out by the capability of iron to replace copper in its salts, as in the production of cement copper. An ideal process would be to win pure copper direct from the ore by using the ore as an anode (the electrode at which oxygen is evolved if the anode be non-oxidisable, or utilised in oxidising and dissolving the anode, in the contrary case), and thus bringing the copper into solution, to be deposited again as metal, free from the other constituents of the ore, on the cathode. The difficulty of completely extracting the crude ore, by reason of the obstruction caused by the insoluble gangue and other constituents, renders this process impracticable. Even when the ore is first smelted to a matte (*e.g.*, coarse metal), and used as an anode, the same difficulty arises. Consequently, there are at present only two classes of process employed to any extent in treating copper electrolytically, viz.:—(1) extraction of the ore as in a wet process, followed by the electrolysis of the cupriferous liquor; and (2) refining of crude copper of the grade of blister metal or black copper.

1. **Extraction and Electro-deposition.**—A typical process for winning copper from the ore electrolytically is that of Siemens

and Halske. In this an ore containing copper as sulphide is leached with a solution of ferric sulphate obtained at a later stage of the process;

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S.$$

The liquor, containing copper sulphate and ferrous sulphate, is circulated first through the cathode compartments of a series of electrolytic tanks, and then through the anode compartments. In the former the copper is deposited on thin copper cathodes, and in the latter the ferrous sulphate, coming from the cathode compartments, is oxidised to ferric sulphate as it passes the anodes, which are of carbon. The solution of ferric sulphate is then used as described above for extracting the ore, the process thus being continuous.

In Hoepfner's process a solution of cupric chloride and sodium chloride is used in extracting the ore, by which means a solution of cuprous chloride in sodium chloride is obtained. Half of this passes to the cathode compartments, and half to the anode compartments. In the former copper is deposited, and in the latter cuprous chloride is converted into cupric chloride by the chlorine equivalent to the copper deposited upon the cathode. The cupric chloride solution is used to extract more ore, diluted with spent liquor (containing only sodium chloride), from the cathode compartment, again divided into two parts, and the cycle of operations repeated. The rationale of the reduction of cupric chloride to cuprous chloride by the copper sulphide in the ore, according to the equation given by Hoepfner,

$$CuS + CuCl_2 = Cu_2Cl_2 + S,$$

has not been satisfactorily explained.

If, in leaching copper ores for an electrolytic process, the copper can be obtained in the cuprous state—that is, already on its way to reduction to metal—a sensible advantage accrues, as the current necessary for its complete reduction is correspondingly diminished.

2. **Electrolytic Refining.**—The refining of copper by electrolysis is a simpler matter than its winning by this means, and is more largely practised. The metal is obtained, by dry processes, as black or blister copper (containing 97 to 98 per cent. Cu), and cast into plates which are used as anodes in a bath of copper sulphate acid with sulphuric acid. The metal is dissolved by the action of the current, and deposited on the cathodes, which are thin sheets of pure copper. As the process consists solely in the transference of copper, and not in its true reduction, the only consumption of electrical energy is in overcoming the resistance of the bath. On this account a pressure of 0·1 to 0·2 volt suffices; a current density of about 10 amperes per square foot is generally used, as when the work is done at a higher rate, irregular deposition and spongy copper result. Some of the impurities in the

crude copper—*e.g.*, iron—go into solution as sulphates and gradually contaminate the electrolyte, until it has to be purified or renewed. Others—*e.g.*, gold, silver, and lead—remain as an insoluble sludge, from which the valuable constituents can be recovered. An improvement in working arrangements, much practised in America, consists in directly connecting only the end plates of a series with the dynamo used for yielding the current, and allowing the intermediate plates to hang free in the bath, one side of each acting as anode and the other as cathode, in regular order, according to the drop of voltage of the current from anode to cathode. This device saves numerous connections and allows of the complete immersion of the plates. The ultimate effect is the conversion of each plate of crude metal, by continual deposition of pure metal on one side (functioning as cathode), and removal of crude metal from the other (functioning as anode), into a plate of pure metal.

USES OF COPPER.—The utility of this metal largely depends on its malleability and ductility, and it is on account of these properties, as well as on account of its fairly high tenacity and resistance to corrosion, that copper is used for tubes, fireboxes, wire, and cooking vessels. Its high electrical conductivity adapts it for the construction of electric leads. It finds an extensive use in making alloys (see below). Its specific gravity is 8·9; it melts at 1,050° C. = 1,922 F.

INFLUENCE OF IMPURITIES ON COPPER.—On account of the existence of two distinct methods of refining copper—viz., the dry way and the electrolytic process—copper commercially employed may be divided into two classes—(1) that which contains a small, but still perfectly perceptible, amount of impurity, and (2) that which is almost chemically pure. The most characteristic impurity of the former is oxygen, which is intentionally left in the metal by stopping the poling process before complete reduction has been effected. Seeing that pure electrolytic copper, though somewhat soft, has a high tensile strength (up to 20 tons per square inch), is very ductile, and altogether reliable as a material of construction, the presence of oxygen in pure copper is not necessary to improve it. On the other hand, copper prepared by the dry process, and free from oxygen, is deteriorated in these same properties by amounts of foreign matter that are of little moment when a suitable quantity of oxygen is also present. Recently, Hampe has examined the effect of the addition of known quantities of such foreign elements as are found in copper prepared in the dry way, to pure electrolytic copper, and has found that the tensile strength and ductility are not appreciably impaired by arsenic and antimony up to 1 per cent. According to Roberts-Austen, bismuth, even 0·1 per cent., causes the copper containing it to be of low tensile strength and brittle.

It is generally conceded that sulphur, bismuth, lead, and possibly iron have an injurious effect upon the mechanical properties of commercial copper. The same appears true of antimony but not of arsenic. Nickel, which is constantly present in commercial copper, seems to have a hardening influence, but is not otherwise objectionable. It may be taken that when any of these harmful impurities in its elementary state is present in copper, its effect is more serious than when sufficient oxygen is present to retain the said impurity as an oxide. For this reason an impure copper poled to tough pitch will contain more oxygen (needed to counteract the effect of the impurities) than an approximately pure copper of the same mechanical properties will contain. Where copper has to withstand heavy wear, as in locomotive fire-boxes, a pure soft metal is possibly less advantageous than one somewhat harder from the presence of such impurities as arsenic and nickel.

For use as an electrical conductor, on the other hand, electrolytic copper is employed, as its conductivity is equal to, or exceeds, Matthiessen's standard taken as 100,* whereas copper made by dry processes has a conductivity ranging from 90 down to 50, on the same scale. The greatest effect in lowering the conductivity is that due to arsenic, 0·1 per cent. of which may lower it to 50; tin is similarly deleterious.

COPPER ALLOYS.—Brass.—Alloys of copper and zinc, ranging from 88 of copper and 12 of zinc to 50 of copper and 50 of zinc, may be classed as brass. The only two definite compounds of copper with zinc which appear to exist, have the formulæ Zn_2Cu and $ZnCu_2$. Alloys with large proportions of copper or zinc may be regarded as solidified solutions of these alloys in the metal which is in excess. Ordinary qualities, of definite yellow colour, range between 60 copper to 40 zinc and 75 copper to 25 zinc. Strong brass, capable of being readily worked and used for such purposes as the tubes of locomotive boilers, contains 70 per cent. of copper and 29·5 per cent. of zinc, the balance being lead with traces of iron and other impurities. Another grade, much used, contains 66 per cent. of copper and 33 per cent. of zinc, corresponding with the formula Cu_2Zn. Brass is generally made in crucibles, for which a reverberatory furnace may be substituted. The ingots of copper are made red-hot, then melted in the crucibles and the zinc added. It is advantageous to first melt some scrap brass in the crucible, together with a little fluor spar, or other flux, the copper being then added. A slight surplus of zinc is needed, both to combine with any oxygen in the copper and to compensate for loss by volatilisation. The purest obtainable copper and zinc are used, the presence of arsenic and of iron to the extent of more than

* Based on the conductivity of the purest silver available at the time of the preparation of the standard.

0·2 per cent. being considered objectionable. The addition of 1 to 2 per cent. of lead is sometimes practised in making brass castings, which have afterwards to be turned.

Gun metal is essentially a copper-tin alloy, though lead and zinc may be present. The definite copper-tin alloys present in gun metal and bronzes have been found to have the formulæ Cu_9Sn, corresponding with 61·64 per cent. Cu, and Cu_4Sn, corresponding with 68·18 per cent. Cu. The alloys in use are solidified solutions of these compounds (which are white and brittle) in excess of copper. Gun metal originally used for ordnance consisted of 91 per cent. Cu and 9 per cent. Sn, but since it has ceased to be employed for this manufacture, these proportions have undergone considerable variation; thus, 87·5 per cent. Cu to 12·5 per cent. Sn is a common proportion; alloys with 16 to 18 per cent. of tin, 80 of copper, 2 to 4 per cent. of lead and zinc are generally used for strong castings and bearings.

Bell metal is a resonant alloy with about 78 per cent. Cu and 22 per cent. Sn.

Bronzes.—These are also copper-tin alloys, varying from the material used in this country for bronze coinage (Cu 95 per cent., Sn 4 per cent., Zn 1 per cent.) to alloys containing as much as 16 per cent. Zn. "Phosphor-bronze" has the composition Cu 82 per cent., Sn 13 per cent., Pb 4 per cent., P 0·5 per cent.; while "silicon bronze" is copper containing 1 to 2 per cent. of zinc and tin and a mere trace of silicon. Both alloys are a good deal used for telegraph and telephone wires. **Manganese bronze** has the composition Cu 81 per cent., Mn 17 per cent., iron 1·5 per cent., and is used for ships' propellers; alloys containing from 3 to 15 per cent. Mn are also used. Much "manganese bronze" is free from manganese.

Delta metal is a ferruginous brass containing about Cu 55 per cent., Zn 43 per cent., Fe 1 per cent., with traces of lead and phosphorus. **Bull metal** is a similar alloy. Both alloys are used as substitutes for gun metals and bronzes (see also pp. 20-23).

LEAD.

It is doubtful whether lead ever occurs native. The following are the chief ores of the metal:—

Galena (lead sulphide, PbS).—This is the most abundant and almost the only important ore of lead. Pure specimens of this mineral consist of cubical crystals which have a metallic lustre and a specific gravity of 7·5. Galena may be associated with silver sulphide without undergoing change of form. The presence of a very small quantity of silver—*e.g.*, 0·1 to 0·2 per cent.—constitutes the ore an argentiferous galena, but, as will be seen later, even smaller percentages may be remuneratively extracted. Galena frequently also contains gold.

Antimony is a common impurity of the mineral. The gangue in which galena is found is usually quartz, calcite, fluor spar or heavy spar. Ores of copper and zinc often accompany galena. The principal lead mines of this country are those of Alston Moor, in the north of England, and of Derbyshire. The Scotch and Welsh mines are also of importance. The largest supply of lead is, however, obtained from America, both from the United States and Canada. The German deposits in the Harz and those of Spain and Australia are also considerable. Lead is, indeed, widely distributed throughout the world.

Cerussite (lead carbonate, $PbCO_3$) is extensively worked at Leadville, Colorado, where it is associated with galena. It occurs both amorphous and crystalline, and in the latter condition is sometimes black from the presence of lead sulphide.

Anglesite (lead sulphate, $PbSO_4$).—Originally found in Anglesea, whence its name. It is not abundant, though deposits occur in this country, Australia, and Peru. The mineral is often rich in silver, containing 30 to 100 ozs. of silver to the ton.

Many other lead compounds, such as the double chloride and carbonate, $PbCl_2.PbCO_3$, the chromate and the double chloride and phosphate are also found, but their comparatively small quantity renders them of little industrial importance.

It is usually found that the oxidised ores of lead—*e.g.*, lead oxide, carbonate, and sulphate—occur in the superficial lodes lying above those carrying galena. The same is true of zinc and copper ores, the cause of the phenomenon being the weathering of the original sulphides.

Preparation of Lead Ores for Smelting.—The substances constituting the gangue of the galena must be removed as far as possible before the ore is smelted, both because they occasion a loss of lead as fume and slag (dealt with in the description of the smelting of the ore—*v.i.*), and because the metals contained in them find there way into the finished lead. The main fact on which the concentration of lead ores is based, is that the galena has a higher specific gravity than the gangue. The ease with which the various constituents are separated depends, *pari passu*, on the difference of their specific gravity (galena 7·5, heavy spar 4·5, copper pyrites 4·3, blende 4·1, quartz 2·6). Mechanical separation resting on difference of specific gravity can only be applied when the gangue is intermixed with, but not disseminated through the galena, as the latter condition would necessitate reduction to a very fine state of division. The process of concentration is carried out by roughly crushing the ore and washing in a stream of water, the specifically lighter gangue being thus removed. When, however, argentiferous galena, containing its silver distributed through the gangue instead of being in combination with the galena, is worked, concentration may cause serious loss of the more costly metal.

The methods in use for smelting galena may be divided according to the reactions on which they depend.

1. **Partial Roasting and Self-Reduction.**—This is similar to that already described under copper (*q.v.*). When lead sulphide is roasted, it is partly converted into oxide with elimination of SO_2, and is partly directly oxidised into lead sulphate. Both oxide and sulphate are capable of reacting with lead sulphide (left when the roasting is incomplete) in the following manner:—

$$PbS + PbSO_4 = 2Pb + 2SO_2.$$
$$PbS + 2PbO = 3Pb + SO_2.$$

These reactions have lately been disputed, but no satisfactory counter evidence has yet been offered.

2. **Complete Roasting and Reduction by Carbon.**—This process consists in roasting galena until the bulk of the lead is converted into oxide, though some passes into sulphate, and reducing it in cupolas or blast furnaces with carbon. The complete reduction of lead silicates that may be formed by the action of the lead oxide upon the siliceous gangue, is aided by the presence of iron ores naturally associated with the lead ores which are smelted in this manner. The action of the iron ore is probably due to the tendency of oxide of iron to form silicates, and thus, in the presence of carbon, to liberate lead from its silicates.

3. **Reduction by Iron** (*"Precipitation Process"*).—In this process the sulphur of the galena is removed as iron sulphide, the lead being directly obtained in the metallic state.

The various methods thus catalogued may be dealt with as follows:—

1. **Self-Reduction.**—The first of the above methods is that generally employed in this country, and is typified by the Flintshire process. This is always conducted in a reverberatory furnace, shown in Fig. 21. It differs from ordinary furnaces of this kind in that the hearth is made from slag produced during the smelting, shaped into a depression or well, B, in the centre. The shaping is performed while the slag is hot and plastic, and the form is retained during the succeeding operation. The flame from the hearth of the furnace, F, passes over the fire-bridge, and is deflected on to the charge, which is introduced through the hopper, T, and is worked through the side doors, *o*.

About a ton of ore is charged into the hot furnace and immediately spread over the hearth and stirred, while the air supply is carefully regulated until the charge has become pasty. During this part of the process the oxidation of a portion of the galena to lead oxide and sulphate takes place. Air is then excluded from the furnace, and the temperature is maintained at redness in order that the reaction of the sulphide with the oxide

and sulphate respectively may proceed. The charge runs down into the well, where the lead collects at the bottom. The undecomposed ore and slag are chilled by opening the furnace doors, and, when semi-solid, pushed back on to the higher part of the hearth near the fire-bridge. The temperature is again raised until the charge runs down a second time, a fresh quantity of lead being reduced. The slag must now be rendered less fusible—*i.e.*, it must be "dried up" by throwing lime into the furnace. It is then sufficiently pasty to be again pushed back on to the higher part of the hearth, where it may now be again calcined. A third fusion follows, and should over-oxidation have occurred, a little coal is added to the charge as a corrective. The charge is now ready for withdrawal, save that there is lead disseminated through the slag. To recover this, another portion of lime is thrown in, and the pasty product pushed back on to the upper part of the hearth

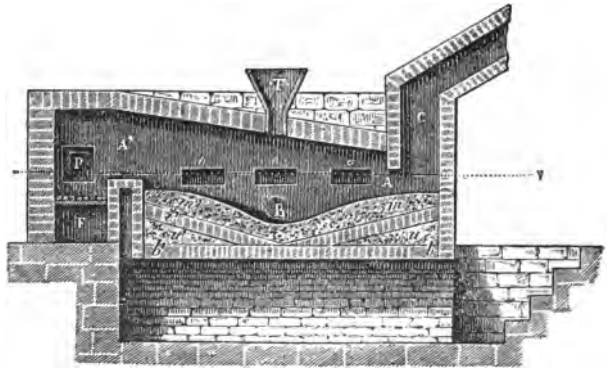


Fig. 21.—Furnace for smelting galena.
F, Hearth; T, hopper; *o*, side doors; P, stoking door.

to drain. The crude lead is now run from the well into a tapping pot. Much dross collects on the surface of the molten metal in the pot, and before removing this, the entrapped lead must be shaken out of it by agitation with a paddle and the introduction of small coal, the gases from which are ignited, the heat thus generated melting the metal in the dross. The lead is then ladled into pigs. Working with an ore containing 75 to 80 per cent. of lead a yield of 65 to 70 per cent. of lead is obtained, the balance being recovered by working up the slag and fume.

During these operations a good deal of lead oxide is volatilised, and, together with volatile impurities such as zinc, arsenic, and oxide of antimony, constitutes flue-dust.* The quantity of

* Hannay has asserted that the production of fume is dependent on the formation of compounds of SO_2 with PbS, stable at a high temperature, but dissociated on cooling. Evidence in this direction is still inconclusive.

such dust is greater the greater the quantity of volatile impurities, which carry over less volatile constituents of the charge. Lead fume is condensed by using very long flues (sometimes more than a mile in length). This length can be diminished by the use of various condensers, in which the fume is either pumped through water or submitted to the action of a water spray. The fume contains 60 to 80 per cent. of lead sulphate, small quantities of lead sulphide, lime, and zinc oxide.

The condensed fume is worked up with another charge. It is poorer in silver than is the original ore.

It is in some places customary to carry out the self-reduction process on a hearth supplied with an air blast, known as the Scotch or ore hearth. This is a rectangular cast-iron box, A (Fig. 22), with a twyer, B, entering at the back. At the front

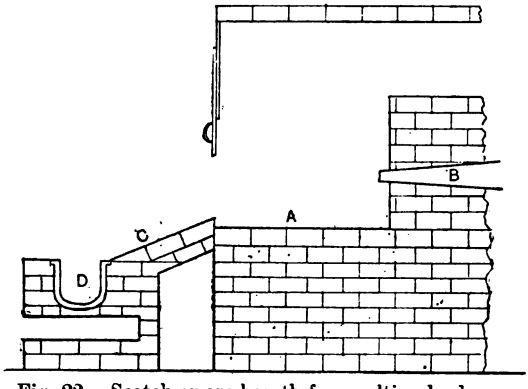


Fig. 22.—Scotch or ore hearth for smelting lead ores.
A, Iron box; B, twyer; C, work-stone; D, melting pot.

of the box an inclined iron plate (the "work-stone"), C, slopes away from the furnace to the melting pot, D, which is kept hot by a separate fire. The furnace is first filled with coal, which is kindled. The ore is thrown on and partially roasted by means of the blast. From time to time much of the charge is drawn on to the work-stone, where the glassy "grey slag," rich in silicate of lead, is separated from the unreduced ore and unburnt fuel, and put aside for treatment on the slag hearths (*v.i.*). During this selection the lead already reduced runs down a channel provided for it on the work-stone, and into the melting pot. The clinkered mass of fuel and ore, *browse*, is returned, fresh ore and fuel added, and the process continued. It is obvious that in this process the reducing action of the fuel plays a part, as distinct from the self-reduction of the ore.

The slags from both the Flintshire and the Scotch process are worked up in slag hearths. The general object is to reduce

the lead from the lead silicate. For this purpose the slags are heated on a hearth with the aid of a blast, the proportion of acid to basic oxides being so adjusted as to yield a fusible slag irrespective of the decomposition of the lead silicate. The lead oxide is thus free to be reduced, and the lead is allowed to trickle away through a filter bed of cinders into the lead pot. The product, *slag lead*, is hard, impure, and of low grade.

Bessemerising Galena.—Recently, selective oxidation in a converter, in the manner already in use for iron (see *Bessemerising*, p. 142), and in smaller degree for copper (p. 163), has been applied to lead.

2. **Reduction by means of Carbon.**—This method of winning lead is carried out in cupolas or small blast furnaces. The process is especially adapted for poor lead ores (which have been roasted fairly free from sulphur) rich in silica, and is analogous to the reduction of iron in the blast furnace, the main point of difference being the substitution of ferrous oxide for lime as a flux for the siliceous gangue. The blast furnace is of various forms, being either rectangular or circular in section, and is usually of nearly uniform diameter throughout its length. The bottom or hearth of the furnace is fitted with twyers. The burden of roasted ore, coke, and flux—frequently iron ore, together with limestone—is introduced at the throat, from which the fumes are drawn off into condensing flues. Metallic lead and slag rich in ferrous silicate are produced. It thus appears that the ferruginous matter is reduced to the ferrous state and forms ferrous silicate with the silica of the lead silicate, the lead being simultaneously reduced to the metallic state by the carbon of the fuel, the presence of which determines the replacement of lead oxide, in its silicate, by ferrous oxide.

3. **Reduction by Iron** (so-called *precipitation process*).—The fundamental reaction upon which this process depends is expressed by the equation—

$$PbS + Fe = FeS + Pb.$$

In its simplest form this method consists in charging a reverberatory or blast furnace with galena and scrap iron (together with fuel in the case of the blast furnace), and raising the temperature until the above reaction sets in. The products of the process are metallic lead, a matte consisting of sulphides of iron, lead, and any copper and silver that may be in the ore, and a slag consisting chiefly of silicates of iron. The matte is roasted and returned with the next charge, the operation being repeated until the copper content is 15 to 20 per cent., when the matte is worked up as coarse metal (see *Copper*, p. 158). It is economical to substitute oxidised ferruginous matter—*e.g.*, iron ore, burnt pyrites, and iron silicates from copper smelting (*q.v.*)—for metallic iron. The carbon of the fuel reduces these sub-

stances, and the metallic iron thus produced removes the sulphur from the lead sulphide.

The products of the well-known Freiberg process—which is mainly notable for its highly systematic method of working, whereby the whole of the valuable constituents of the ores treated—viz., Pb, Zn, Bi, Ag, Au, As, $CuSO_4$, $FeSO_4$, $MnSO_4$, Ni, and Co as arsenides, As_4O_6, As_2S_3 and As_2S_2, are recovered—are similar to those mentioned above, a crude or "work-lead," a matte and a slag being produced, and occasionally a *speiss* rich in nickel, cobalt, silver, and arsenic. In these processes an alternate roasting to remove sulphur, and reduction of the resulting oxide, are the characteristic features, a fraction of the lead being obtained by each pair of operations.

Treatment of Crude or Work Lead (*Werk-blei*).—The chief impurities in crude lead are antimony, copper, arsenic, bismuth, silver, and iron. An analysis of a Freiberg crude lead (from an arsenical ore) is as follows :—

	Per cent.
Lead, ...	97·72
Arsenic, ...	1·36
Antimony, ...	0·72
Iron, ...	0·07
Copper, ...	0·25
Silver, ...	0·59

Two of the most desirable qualities of lead are its softness and plasticity, properties which are impaired by the presence of impurities. Most of the impurities of lead (except silver) are more oxidisable than the metal itself. The process of **improving** or **softening** consists in exposing the molten lead to an oxidising atmosphere. The furnace used for the purpose is of the reverberatory type, with a hearth consisting of a cast-iron pan. The pig lead is melted, run into the pan and allowed to remain in an oxidising atmosphere. The dross which rises to the surface is raked off from time to time, until a sample ingot of the lead shows a crystalline surface. The lead in the dross is recovered by reduction with coal, and is sufficiently rich in antimony to be sent to the type foundry. When the lead is rich in copper, it is advantageous to *liquate* it before improving. A liquation furnace is a reverberatory furnace with a hearth which slopes from the fire-bridge downwards, and terminates in a well. The pigs of lead are placed at the top of the slope, and the temperature so regulated as to little exceed the melting point of lead, which flows down into the well, leaving behind the less fusible impurities, such as copper—sulphur and arsenic being also partially separated in combination with the metallic impurities.

Processes for Desilverising Lead.—The removal of silver from lead may be effected by taking advantage of the fact that lead is more easily oxidised than silver, as in the laboratory method of silver assay. Inasmuch as it is in this case necessary

to subsequently reduce the lead oxide formed, such a process can only be profitable when the lead is comparatively rich in silver. This is the principle of the process formerly in use. It is now customary, however, to submit the argentiferous lead to a concentration process, whereby an alloy rich enough to be profitably oxidised by cupellation can be obtained. There are two distinct methods for this purpose in use.

Pattinson's process depends upon the fact that when a bath of argentiferous lead is allowed to cool gradually, crystals of lead poorer in silver than the rest of the bath first form. This condition obtains until the lead contains 600 to 700 ozs. of silver to the ton, when such spontaneous segregation ceases. So small a quantity as 2 to 3 ozs. of silver to the ton of lead may thus be extracted, although the limit for profitable working depends on the market price of silver. The Pattinson plant (Fig. 23) consists of a series of cast-iron pans, holding 10 to 20 tons each, represented in the diagram above. Each is heated by its own furnace. The lead to be desilverised is run into a pot near the

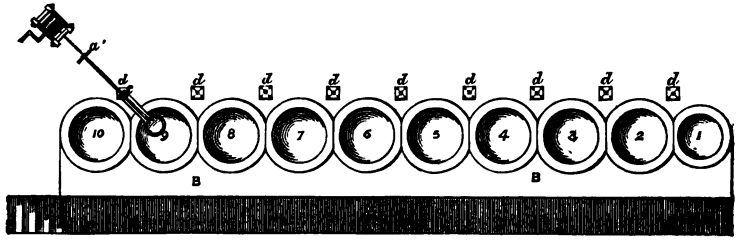


Fig. 23.—Plant for Pattinson's process.

middle of the series—*e.g.*, No. 5. The lead is kept melted for a short time, skimmed from dross, and is then chilled, sometimes by sprinkling water on the surface, and the cake of solidified lead broken up with a "slice" and stirred into the bath. The stirring is continued until $\frac{1}{3}$ to $\frac{1}{2}$ has solidified, according to whether the "high" or "low" system (*v.i.*) is being used. The crystals poorer in silver than the original lead are now fished out by means of a perforated ladle, *a*, working on the block, *d*, as a fulcrum, and transferred to pot No. 6, while the liquid portion is transferred to pot No. 4. A fresh batch of lead of the same content of silver as that previously used is run into pot 5 and the process repeated until pots 6 and 4 contain sufficient lead to allow of their contents being fractionated in the same way, the poorer lead of each fractionation going to the pot immediately to the left and the richer to the right.

It will thus be apparent that the extreme right-hand pot ("rich pot") will be continually receiving lead rich in silver, and the extreme left-hand pot ("market pot") is continually

receiving lead almost completely desilverised—*e.g.*, containing only ½ oz. Ag per ton, and ready to be cast into marketable pigs. It is obvious that as there is a regular gradation of content of silver throughout the series of pots, crude lead of any content of silver can be worked up together with another of a different content by starting each in its appropriate pot. In the high or ⅓ system, the content of silver is approximately doubled at each separation. In the lower or ⅛ system the increase of silver content is about three fold at each step. The low system is particularly applicable to the treatment of comparatively rich lead.

The dross formed is worked up with lead slags in the manner already described. An incidental advantage of the Pattinson process is that it is an improving process apart from its use for desilverising. This results from the free exposure of the melted lead to the air. This double function causes the use of the Pattinson process in white lead making, where the purity of the lead is essential for success. In some cases a single pot is used, provided with draining grates and an inlet for steam. Repeated crystallisations are carried on as in a Pattinson battery of pots, steam at 50 lbs. pressure being admitted to take the place of hand stirring with a slice, and the still molten rich lead is tapped off, leaving the crystals on the grating. It is claimed that the steam equalises the crystallisation better than stirring does, and at the same time improves the lead by provoking limited oxidation.

Parkes Process.—This method is an example of the purification of a metal by extraction with an immiscible solvent. It depends upon the fact that fused lead and zinc are not miscible in all proportions, but each dissolves the other to a limited extent,* and that zinc alloys more easily with silver than does lead. Thus, when zinc is melted in a bath of argentiferous lead, a partially oxidised alloy of lead, zinc, and silver rises and solidifies, constituting a scum on the lead. The process is conducted in pots, a section of one of which is represented in Fig. 24. Contrary to the requirement of the Pattinson process, which is that the temperature shall be maintained at or near the fusing point of lead (325° C. = 617° F.), the bath in the Parkes process is kept somewhat above the melting point of zinc (415° C. = 779° F.) in order to ensure perfect admixture. The lead is charged into a pot, A, where it is melted; an ingot of zinc is then thrown on the surface, and when this is fused the rest of the zinc is added, the quantity necessary depending upon the richness of the lead in silver, and varying from 1¼ to 2 per cent., though in modern practice as much as 6 per cent. is often used. The whole is then stirred, either mechanically or by the admission of steam, in which case a high temperature must be

* At 400° C. = 752° F., lead dissolves 0·8 per cent. of zinc; zinc, at its fusing point, dissolves 1·5 per cent. of lead.

avoided lest the steam oxidise the zinc. After the stirring has been continued for half an hour, the fire is damped down and the crust of zinc-lead-silver alloy, termed technically *zinc amalgam* (containing, for example, Pb 55 per cent., Zn 40 per cent., Ag 5 per cent., mixed with oxide),* is allowed to solidify, and removed with a perforated ladle. The lead is then baled out or removed by the pump, B, which consists of an iron cylinder fitted with a valve, C, opening inwards, an exit tube, D, and a steam admission tube, E. The molten lead lifts the valve, C, and finds its level in the cylinder, B, being then driven by steam pressure up the exit tube, D, into the delivery tube, F, whence it flows into the pig mould, G. When the lead in the cylinder has all passed over, the pressure of steam is automatically relieved through the exit tube, D; lead again flows into the cylinder, and the process

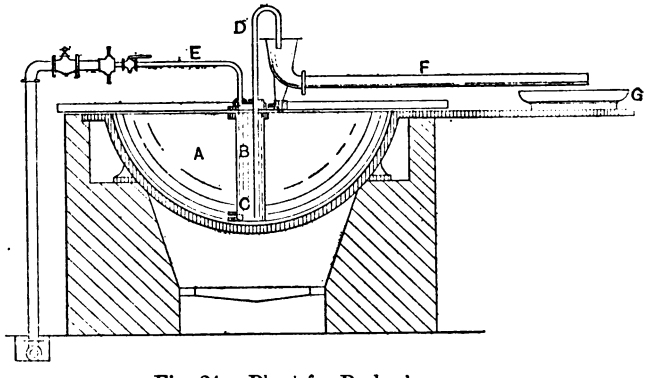


Fig. 24.—Plant for Parkes' process.

A, Melting pot; B, pump; C, valve; D, exit tube; E, steam admission tube; F, delivery tube; G, pig mould.

is repeated, the emptying action being almost continuous. The removal of the small quantity of zinc which remains dissolved in the lead is a difficulty of the process, and several methods have been adopted. Treatment in an improving furnace (*v.s.*) has been used. Another plan consists in stirring the zinciferous lead with lead chloride which converts the zinc into $ZnCl_2$, an equivalent of lead being reduced. Steam may also be used to oxidise the zinc, or an oxidising fusion in a blast furnace may be adopted.

The zinc alloy skimmed off is first liquated to remove most of the lead. The lead goes back to the Parkes pots, and the remaining alloy (Zn and Ag) is heated in a distil-

* It is claimed that the presence of a small proportion of aluminium (0·5 per cent.) in the zinc used will much diminish the proportion of oxide in the alloy.

lation crucible (see *Zinc*), together with wood charcoal, zinc from the alloy and from the oxide being thus recovered.* The residue is then worked up for silver (*q.v.*). At some works—*e.g.*, at Freiberg—the Pattinson and Parkes processes are combined, the former being used until the rich lead contains only 50 ozs. of silver per ton, when it is treated by the latter.

The subject of cupellation—*i.e.*, the separation of silver when present in considerable amount from lead, by the oxidation of the latter, will be dealt with under *Silver*.

Electrolytic Refining of Lead.—When lead is rich in silver (*e.g.*, contains as much as 180 ozs. per ton) it is said to be capable of profitable refining by electrolysis. For this purpose, thin plates of the lead are enclosed in sacking, and serve as the anode of an electrolytic cell charged with a solution of lead sulphate in sodium acetate, and heated to about 40° C. = 104° F. The cathodes are of pure lead. The lead deposited on these soon strips off and falls to the bottom of the bath. When the anodes have nearly dissolved, the gold and silver which have collected in the bags may be worked up. The lead need not be "improved" previous to refining.

Uses of Lead.—For the use of lead as a structural material, and for its employment to resist mineral acids (*e.g.*, in vitriol chambers), see the sections allotted to these subjects, Vol. II.

Commercial lead is one of the purest metals industrially prepared, as may be seen from the following analysis:—

Lead,	99·9837	per cent.
Copper,	0·0014	,,
Antimony,	0·0037	,,
Zinc,	0·0016	,,
Iron,	0·0016	,,
Silver,	0·0080	,,
	100·0000	,,

Most of the impurities of lead tend to harden it. The specific gravity of the pure metal is 11·35, and the melting point is 325° C. = 617° F.

Lead Alloys.—The principal alloys of lead are those with tin, antimony, and arsenic. The lead-tin alloys have a greater tenacity and are more fusible than either metal. Thus **pewter** (20 per cent. Pb, 80 per cent. Sn) is a strong alloy not easily corroded, the safety of which for drinking vessels is impaired if the proportion of lead be sensibly increased. Common **solder** (tin solder) consists of equal weights of lead and tin; plumber's

* Electrolytic refining of the alloy has recently been attempted. The alloy is cast into slabs to serve as anodes, from which the zinc is to be electrolytically dissolved and re-deposited, leaving the silver and lead. It is, however, difficult to deposit zinc electrolytically from any but an alkaline bath.

solder 2 parts by weight of lead to 1 of tin (see p. 37). Fine solder has the composition 2 of tin to 1 of lead. These alloys have a lower fusing point than either constituent has—*e.g.*, common solder melts at 190° C. = 374° F.—but the fusing point rises with the percentage of lead when the proportion 1 of lead to 2 of tin has been exceeded.

Type metal contains 70 per cent. of lead, 18 per cent. of antimony, 10 per cent. of tin, and 2 per cent. of copper. **Stereotype metal** has 82 per cent. of lead, 14·8 per cent. of antimony, and 3·2 per cent. of tin. The function of the antimony in these alloys is to produce a metal hard enough to withstand the pressure of the printing machine. **White metal** is also lead hardened with antimony, and containing tin—*e.g.*, 60 per cent. Pb, 20 per cent. Sb, 20 per cent. Sn. For making shot for sporting guns, lead is slightly hardened by arsenic, which also appears to favour the assumption of sphericity by the drops of melted metal as they fall down the shot tower. They are commonly blackened by reception in a solution of sodium sulphide, or by tumbling with graphite. On account of the low fusing point and plasticity of lead, it can be formed into rod and tube by forcing it, while just at its melting point, through a die, plain for rod and cored for tube. To obtain a harder tube than is afforded by pure lead (*e.g.*, "compo." tube) some antimony is commonly added.

ZINC.

Zinc does not occur native. Its chief ores are as follows:—

1. **Blende** (zinc sulphide, ZnS).—This mineral occurs associated with sulphides of lead, iron, and copper; it is usually black (whence the mining name "black-jack"), from the presence of these impurities, and lustrous. It is the chief source of the metal. Good ordinary samples contain about 50 per cent. Zn; pure ZnS contains 66 per cent. Zn.

2. **Calamine** (zinc carbonate, $ZnCO_3$).—This is also coloured by iron, frequently being brown, from the presence of ferric oxide. It may contain about 40 per cent. of zinc instead of 52, which is the theoretical percentage. An ore consisting of hydrated oxide and carbonate, $ZnCO_3.2Zn(OH)_2$, is also worked.

3. **Zinc Silicates.**—The most abundant of these is **electric calamine**, $Zn_2SiO_4.H_2O$, so called from the fact that it is said to become electric on heating. It is usually white.

Willemite, Zn_2SiO_4, is another zinc silicate which is worked.

4. **Red Zinc Ore** (zinc oxide, ZnO) owes its colour to the presence of oxides of manganese and iron. It may contain as much as 75 per cent. of Zn.

The chief zinc-yielding districts are Belgium and the Rhine country, Silesia, Greece, France, United States, and this country, though the amount obtained here is comparatively small, Cum-

berland, Wales, and the Isle of Man being now the chief districts of supply. Zinc and lead ores are frequently found together and worked in concert.

The **winning of zinc** differs from that of the metals already considered chiefly in the fact that the volatility and heat of combination with oxygen of zinc are greater than those of these other metals (Fe, Cu, Pb). The boiling point of zinc is about 930° C. = 1,706° F., and its vapour is capable of reducing water vapour and carbon dioxide, properties which prevent its being smelted in a blast furnace. It is sometimes, however, feasible to treat ores of zinc in a blast furnace, but only as a means of obtaining a pure oxide; the metal is reduced in contact with the solid fuel of the furnace, volatilised, and burnt again to oxide by the exit gases; the oxide is then collected and reduced in the ordinary way (*v.i.*). The reduction of zinc oxide by means of solid carbon is represented by the equation—

$$ZnO + C = Zn + CO.$$

The decomposition of ZnO absorbs 85 Cal., whilst the formation of CO evolves 29 Cal. Thus the above reaction is endothermic to the extent of 56 Cal., which quantity of heat has to be supplied through the walls of the retort in which the reaction is carried out.

The first step in the treatment of the ore, whether it be blende or calamine, is the roasting of it to oxide. When calamine (zinc carbonate) is treated, it may be roasted, like limestone, in running kilns (see *Lime*), or in reverberatory furnaces; the object of the roasting is to avoid the presence of CO_2, which would oxidise the zinc in the retort in the subsequent distillation process. When blende (zinc sulphide) is roasted, much of it is converted into zinc sulphate, which can only be decomposed at a temperature considerably above that necessary to convert the sulphide into oxide. To avoid the formation of zinc sulphate as far as possible, the blende is coarsely crushed and the roasting is conducted on the hearth of a reverberatory furnace, or, where vitriol is made, in kilns of the Gerstenhöfer type (see *Copper*, p. 156). The roasted ore contains very little zinc sulphate, and, according to Voigt, is free from zinc sulphide, most of the residual sulphur being present as sulphates of lead and calcium, and as calcium sulphide. A considerable quantity of fume is obtained during the roasting; this contains some 10 per cent. of zinc as sulphate, which is leached out and precipitated as zinc carbonate.

The finely-ground calcined ore is mixed with about half its weight of powdered coke or non-caking coal, and the mixture is charged into retorts. These are of two forms, known respectively as the Belgian and the Silesian retort. The former, marked *a* in Fig. 25, are fireclay tubes, either circular or elliptical in section, about 4 feet long, 6 inches internal diameter, and 1 inch

thick in the walls; these are set in an inclined position above the grate of a solid fuel furnace, or in a producer-gas furnace working regeneratively, similar to that used in steel-making (p. 146); the mouth of each retort is fitted with a clay receiver, *b*, to which is attached a sheet-iron pot, *c*, with a small hole for the exit gases; the weight of ore charged is about $\frac{1}{4}$ cwt. for each retort. The latter (Silesian retorts) consist of ⊏-shaped muffles,

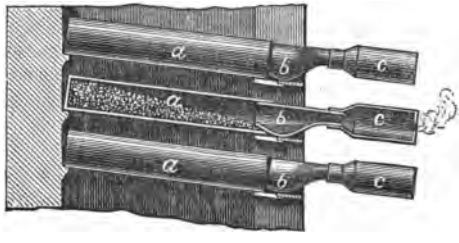


Fig. 25.—Belgian zinc retort.

a, Fireclay tubes; *b*, clay receiver; *c*, pot.

4 to 6 feet long, 8 inches wide, and 18 inches in height, each taking a charge of about $\frac{3}{4}$ cwt.; the front part of the muffle, A (Fig. 26), is fitted in its upper half with a clay nozzle, *p*, which is connected with the clay tube, *r*, leading into the sheet-iron adapter, *s*; the lower half of the front of the muffle, *n*, can be removed for the introduction of the charge; the muffles are set

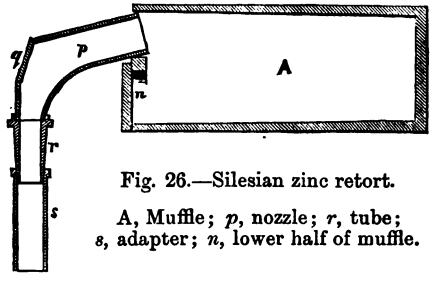


Fig. 26.—Silesian zinc retort.

A, Muffle; *p*, nozzle; *r*, tube; *s*, adapter; *n*, lower half of muffle.

in rows, back to back, in a furnace with a long central grate, or are heated by producer gas with a regenerator in the usual way.

The receivers which are to collect the zinc must be of a temperature to keep it fused. The progress of the distillation is judged by the appearance of the issuing gases. Brown fumes of cadmium oxide first appear, and then zinc vapour, the uncondensed portion of which burns at the end of the condensers until the distillation is complete. Much grey, partially oxidised, and finely-divided zinc collects in the sheet-iron adapters; this is

marketed as **zinc dust** for use as a reducing agent. The yield of fused zinc, or **spelter** as it is commercially termed, is from 70 to 80 per cent. of that in the ore.

Refining of Zinc.—Crude zinc constantly contains lead—*e.g.*, 1 to 3 per cent.*—and often traces of arsenic, cadmium and iron. It is refined by melting on a hearth provided at one point with a well, in which the lead settles out in the course of two or three days, this metal being but sparingly soluble in zinc (see p. 178). The refined zinc above the lead is ladled from the well and cut into ingots. This refining is necessary for zinc that is to be rolled, as well as for that which is to be used for brass making. It is stated that the malleability is not affected provided the lead be below 1·5 per cent., but is much reduced by 0·25 per cent. of iron. Zinc that has been overheated and contains oxide is also unsuited for rolling.

Electrolytic Winning of Zinc.—Several plans have been devised for a wet extraction and reduction of zinc by electrolytic means. Thus, blende is roasted at a low temperature to sulphate, which is leached out with water and the solution electrolysed. Owing to the high chemical energy of zinc, the voltage required to effect its reduction is high (2·5 volts), and waste of energy by the electrolysis of the water of the solution tends to occur. A method proposed by Siemens and Halske is similar to that used by them for copper (p. 167), and consists in extracting blende with ferric sulphate, zinc sulphate and ferrous sulphate being formed and sulphur deposited. During electrolysis the zinc is reduced and ferric sulphate formed, which is again used.

Uses of Zinc.—The specific gravity of zinc is 7; its melting point is 412° C. = 774° F. At the ordinary temperature it is brittle, but at 121° C. = 250° F. it is malleable, so that sheet zinc can be prepared at this latter temperature, and is much used for pipes, gutters, &c., for which it is more advantageous than iron, both on account of its somewhat lower specific gravity and its greater resistance to corrosion. The use of zinc for coating iron has been already dealt with (p. 26). Zinc white is made directly from zinc by burning it (see *Pigments*, Vol. II.), and crude spelter is used, with sulphuric acid, as a cheap source of hydrogen. The application of the metal in primary batteries has been already explained (p. 86).

Zinc Alloys.—Brass has already been considered under copper; the zinc used for making it should be as pure as possible. Zinc-iron alloys (*Zinceisen*) may be prepared by immersing clean iron sheet in a bath of zinc heated to near its boiling point, and are also obtained as bye-products in zincing (*galvanising*; p. 26). They are used as convenient means for introducing iron into special copper-zinc alloys, such as Delta and

* Lead is somewhat volatile in presence of zinc, and, therefore, distils over with the latter in the reduction process.

Bull metal. Zinc-antimony alloys are used for thermopiles. The behaviour of zinc-lead alloys has been dealt with under the desilverising of lead by the Parkes process.

CADMIUM.

This metal accompanies zinc in almost all specimens of its ores. It distils over with the first portions of the zinc, and when this is sufficiently rich (2 to 10 per cent. Cd) it is mixed with coal and distilled in retorts heated to dull redness. A second distillation is necessary to obtain approximately pure cadmium. Cadmium is a metal standing in many respects between zinc and lead. It is soft enough to mark paper faintly; it melts at 320° C. = 608° F., and boils at 770° C. = 1,418° F., and has a specific gravity of 8·6. It is used as a basis for cadmium yellow (CdS; see *Pigments*, Vol. II.), for making **fusible alloys**, *e.g.*, **Wood's metal** (see *Bismuth*), and latterly for electro-deposition as an alloy with silver in place of ordinary silver plating.

TIN.

Tin does not occur native. The following are its ores :—

Tinstone or **Cassiterite.**—This ore consists of crystals of stannic oxide (SnO_2), generally occurring as masses in lodes, or disseminated in very small veins through granitic rock. The denudation of the rocks carrying tinstone has given rise to alluvial deposits of the ore in sands, the ore being then known as **stream-tin.** Arsenical pyrites, wolfram, and other minerals accompany the siliceous gangue of the tinstone. Tinstone is sometimes found light in colour, of regular crystalline form, and approximately pure, but is generally dark from the presence of oxides of iron and manganese. Considerable quantities of tinstone are still raised in Cornwall and Devon, but the islands of Banca and Biliton, the Malay Peninsula, and Australia furnish the chief supplies.

Tin pyrites is essentially a triple sulphide of tin, copper, and iron, containing about 26 per cent. of tin, 30 per cent. of copper, 12 per cent. of iron, and 31 per cent. of sulphur. This ore is of minor importance, and generally accompanies cassiterite to some slight extent.

THE WINNING OF TIN.—1. **Preparation of Tin Ores.**—The majority of tin ores are comparatively poor, containing, for example, 1 to 2½ per cent. of metallic tin, and a cheap method of mechanical concentration is, therefore, necessary. Such a method is rendered possible by the fact that the specific gravity of tinstone (6·5) is much higher than that of most of the accompanying gangue (the specific gravity of quartz being 2·7), so that by stamping the ore (see *Gold*) and washing the resulting powder

by a stream of water, the lighter gangue is carried further away by the water than is the heavier tinstone. When the ore contains a good deal of pyrites, as is usually the case, the washing will not serve to remove the pyrites because the specific gravity of this mineral (5·0) is too near that of tinstone. The first concentrate—*i.e.*, the portion heaviest and richest in tin—must, in this case, be roasted in order to convert the sulphides into oxides, and thus reduce the specific gravity of the matter other than tinstone, the washing being then repeated. As in all methods of mechanical concentration, "sizing" of the ore before washing is advantageous, since effective separation is only obtained when the material treated consists of fragments fairly uniform in size (see *Gold*). Another object of this roasting is the removal of arsenic and sulphur, the former being condensed in a series of chambers, and forming the main source of "white arsenic" (*q.v.*).

Modern roasting plant, such as the Oxland and Hocking roaster, consists of a long cylinder slightly inclined towards a grate, the products of combustion from which traverse the cylinder from end to end. The cylinder is slowly revolved and ore fed in at the upper end, being roasted in its passage and falling out at the other end of the cylinder. The upper end of the cylinder opens into condensing chambers for the collection of arsenious oxide. When the ore is sufficiently rich in copper to pay for the process, the roasted ore is washed with dilute acid and the copper precipitated by iron (see *Copper*). Should bismuth be present it is, at the same time, dissolved by the acid (which in this case is hydrochloric acid), and is precipitated by dilution as basic chloride. As stated above, tungsten in the form of **wolfram** (a tungstate of iron and manganese) is sometimes present in tin ores, and on washing is left with the tinstone. This may be removed by fusion with a small quantity of soda ash (Na_2CO_3), whereby the tungsten is converted into sodium tungstate (Na_2WO_4). This may be leached out with water, together with a quantity of sodium stannate, corresponding with the excess of soda ash used. Sodium tungstate has a limited application in dyeing and for rendering light fabrics uninflammable. The purified tinstone has to be further washed to remove the ferric oxide left by the decomposition of the wolfram.

2. **Reduction to Metallic Tin.**—Stannic oxide is easily reduced by carbon at a red heat. The purified tinstone, "black tin," contains about 65 to 70 per cent. Sn in place of 78·7 per cent. in pure SnO_2. It is mixed with about one-fifth of its weight of anthracite breeze, moistened to agglomerate it, and introduced into a reverberatory furnace. On account of the completeness with which the gangue has been removed, the use of a flux is not always necessary, but should the silica present be more than sufficient to combine with the oxide of iron, a little lime or fluor spar is added. After the temperature has been raised for six

hours, the atmosphere being kept a reducing one meanwhile, the charge is raked, and more anthracite thrown in. The temperature is again raised, and the metal tapped off into an adjacent well lined with firebrick. Most of the slag flows out with the tin, and is mechanically removed from the well, the metal being ladled into ingots. The pasty slags which remain in the furnace retain a considerable proportion of tin globules, which are recovered by crushing and washing. The slags that flow out with the tin are again fused with lime, and another fraction of tin recovered. The final slags consist mainly of ferrous silicate.

The use of blast furnaces for reducing tinstone, formerly adopted, is now nearly extinct, save where charcoal is abundant.

3. **Refining of the Tin.**—Crude tin contains Fe, W, Cu, Pb, As, Sb, Bi, and S in varying amounts. In the refining of tin, advantage is taken of its low melting point, 227° C. = 440° F., by the use of a liquation process. The ingots are piled on the higher end of a sloping hearth and maintained at the melting point of tin. The less fusible metals—*e.g.*, Fe and Cu—together with As and S, remain on the hearth (still containing, however, about 20 per cent. of tin), and the bulk of the tin, together with the more fusible metals, such as Pb and Bi, is collected in a pot, where it is poled with green wood; during this process the agitation of the metal by the gases which escape from the wood aerates it sufficiently to oxidise the more readily oxidisable impurities. The metal is allowed to settle in the pot, when the remaining heavier impurities subside, the upper portion being ladled into ingots and marketed as refined tin, containing 99 to 99·5 per cent. Sn.

Grain tin is refined tin which has been heated to a temperature at which it becomes brittle and has been broken into fragments. The less pure grades of tin **(common tin)** are cast from the middle portion of the contents of the pot. The crude tin, whether that left on the liquating hearth or that separated at the bottom of the refining pot, is known as "hard head"; it contains about 60 per cent. Fe, 18 per cent. Sn, 20 per cent. As, and 2 per cent. S, and is re-worked for the tin it contains. An ingot of pure tin should be smooth and rounded, sharp edges and a frosted surface indicating the presence of impurity, and if this be very great the colour may be of a yellow or purple tint.

4. **Uses of Tin.**—The metal is seldom used alone, save for tubes and linings coming into contact with mineral and aerated waters; it is used for this purpose on account of the circumstance that it is one of the metals which are not attacked by water.

Pure tin has a specific gravity of 7·285; its melting point, as already stated, is 227° C. = 440° F. It is brittle at ordinary temperatures, and is too weak as well as too costly (*e.g.*, £60 to £70 per ton) for use as a structural material. It is malleable at 100° C. = 212° F., and becomes brittle again at 200° C. = 392°

F. Its malleability allows of its extension to the form of foil. Much common "tin foil" is, however, made from lead coated on each side with tin and then beaten thin.

The chief application of tin is in the manufacture of tin plate (p. 27). The resistance of the metal to most vegetable and animal juices, and the fact that when it is wiped on to a clean surface of copper it adheres as does solder, renders tin useful for lining cooking vessels. Its chief alloys are gun-metal (see *Copper*, p. 170), pewter (see *Lead*, p. 180), and **Britannia metal** which usually contains about 90 per cent. Sn, 8 per cent. Sb, and 1 to 2 per cent. Cu. **Speculum metal** (for metallic mirrors) is a white, hard, brilliant alloy, of 2 parts of copper and 1 of tin, sometimes hardened by the addition of arsenic; the tin thus hardened will take a good polish and can be electro-plated. Tin-amalgam (from tin foil and mercury) is used for making mirrors and is prepared from tin containing from 1 to 2 per cent. of copper which hardens it.

Other alloys of tin are dealt with under copper and lead. Grain tin is made for the express purpose of producing "chloride of tin" (stannous chloride, used as a mordant), its finely-divided condition aiding its dissolution in hydrochloric acid.

When tin is exposed to very low temperatures its crystals become differentiated and the metal assumes a grey appearance (*grey tin*); its specific gravity in this condition is 5·7, but the metal reverts to its normal state when heated. The spontaneous disintegration of tin which has been observed in cold climates may be accounted for by its conversion into the grey crystalline variety.

ANTIMONY.

Sources of Antimony.—This metal occurs native, to a trifling extent, in massive form, associated with gold, silver, and arsenic. It occurs as sulphide in **grey antimony ore** (*stibnite*). This is the most important ore of antimony, and consists essentially of the sulphide, Sb_2S_3. It resembles galena in colour, but has a lower specific gravity—viz., 4·7. It is found in Australia, Borneo, Japan, Germany, France, and Hungary. The pure sulphide contains 72·8 per cent. Sb; the ores actually worked may contain about 50 per cent.

Oxides of antimony form various minerals, such as **senarmontite**, Sb_2O_3, and **antimony ochre**, Sb_2O_4. **Red antimony** or **kermes mineral** is an oxysulphide, $Sb_2S_3.Sb_2O_3$.

Winning of Antimony.—Antimony ores are usually rich enough to be worked directly, but a concentration process is practicable and has been applied; this depends on the fusibility of antimony sulphide, which can be liquated from the gangue (see *Liquation of Tin*, p. 187). The liquation may be carried out in a reverberatory furnace, or in crucibles with an exit tube from the lower part, or in vertical retorts worked continuously. The

liquated antimony sulphide is called "crude antimony," the metal itself being known as "regulus of antimony." As in the case of lead and copper, the sulphide and oxide of antimony will react with each other at a high temperature, with the production of free metal and SO_2. This is sometimes taken advantage of in the self-reduction process. For this purpose the antimony is roasted until part of it is oxidised to Sb_2O_4, which is then heated in crucibles with raw ore, the following reaction occurring:—

$$3Sb_2O_4 + 2Sb_2S_3 = 10Sb + 6SO_2.$$

It is usual to cover the contents of the pot with a mixture of charcoal and sodium carbonate (or with tartar as an equivalent). It is probable that the reduction may be partly due to the removal of the sulphur by the alkaline carbonate.

The reduction of antimony is more usually effected by the use of iron, as in the so-called "precipitation" process for smelting galena (p. 175).

The ground ore is mixed with about one-third of its weight of wrought-iron scrap (tin plate cuttings), one-tenth of its weight of salt, and some slag from a previous fusion; the mixture is charged into fireclay crucibles, holding about $\frac{1}{2}$ cwt. apiece. A ball of scrap tin plate is put into the mouth of the crucible, a trace of tin in the antimony whitening the metal and improving its crystalline appearance (*v.i.*). Forty such crucibles are introduced through the holes in the roof of a long furnace having a hearth at each end. As the charge melts, the ball of scrap tin is pushed down, and in about three hours the reduction is complete. The main reaction is represented by the following equation:—

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

The contents of the crucible is then poured into an iron mould, and when it has set the slag is knocked off from the metal collected at the bottom. This metal is known as "singles," and contains about 91·5 per cent. Sb, 7 per cent. Fe, and 1 per cent. S. It is broken up and submitted to the process of "doubling," for which about 80 lbs. is charged into a crucible, together with 7 or 8 lbs. of liquated sulphide of antimony and 4 lbs. of salt, which may with advantage be kelp-salt.* The antimony sulphide is added in order to convert the iron of the crude antimony into sulphide, a corresponding quantity of antimony being obtained as metal. The fused mass is skimmed and the metal cast.

This metal contains 99·5 per cent. Sb, 0·2 per cent. Fe, 0·2 per cent. S, and is known as "starbowls."

The process of refining antimony is known as "starring," because the finished metal has a stellate crystalline appearance.

* *Kelp-salt* is obtained in the manufacture of iodine from kelp, and contains some 10 per cent. of sodium carbonate, the balance being chiefly common salt.

It is carried out by freeing the metal obtained in the "doubling" process from slag, and charging about 80 lbs. of it into the crucibles nearest the fire of the same furnace as is used for the preceding operations, together with 8 lbs. of "antimony flux," which consists of crude potash melted with liquated antimony sulphide. This flux removes the remaining Fe and S; the efficiency is to be ascribed to the ease with which thioantimonites and thioantimonates are formed, the alkali sulphide uniting with antimony sulphide to produce these substances. Care is taken not to saturate the flux, during its preparation, with antimony sulphide, so that it may take up its quota from the metal. It is revivified occasionally by the addition of a little potash. The purified metal is cast into ingots, and is known as "star antimony."

Much fume is produced in the smelting of antimony, and is condensed in flues. It consists mainly of oxides of antimony, and contains about 70 per cent. Sb, which amounts to about 10 per cent. of the antimony in the ore treated. It is mixed with coke, and worked up with the ore in melting for "singles."

Antimony is occasionally won by smelting the roasted ore in blast furnaces, a crude metal rich in iron and sulphur being obtained, and refined in the ordinary way. As the antimony in the charge is present chiefly as Sb_2O_3 and Sb_2O_4, but little is volatilised during this process.

Electrolytic Winning of Antimony.—A solution of antimony sulphide in sodium sulphide (sodium thioantimonite), containing a little NaCl to add to its conductivity, is electrolysed in iron cells with iron cathodes and lead anodes. At the cathode the sodium thioantimonite is reduced, and the sodium sulphide thus liberated serves for the dissolution of another portion of antimony sulphide.

Properties and Uses of Antimony.—Antimony is a nearly white, hard, crystalline metal, of specific gravity 6·7; it melts at 630° C. = 1,166° F.* It is stated to exist in an allotropic modification, produced by the slow electrolysis of a strong solution of antimonious chloride. The antimony thus obtained is amorphous and lustrous, and has a specific gravity of 5·78. It becomes crystalline above 77° C. = 170° F., and (with evolution of heat) when scratched. It is never produced free from antimonious chloride. Antimony is but little used alone, save when powdered, in which condition it is employed for bronzing plaster casts; the powder is termed "iron black." Its chief use is in hardening other metals, notably lead and tin for type metal and Britannia metal (*q.v.*). It serves as a basis for the manufacture of salts used in the arts and in medicine, and of its oxysulphide (antimony vermilion), which is used as a pigment (see *Pigments*, Vol. II.).

* Until lately the melting point has been generally much understated.

BISMUTH.

This metal occurs **native** to a considerable extent, native bismuth being indeed its chief source. It is found in masses and in veins; small deposits occur in Cornwall and Cumberland, but Australia and Bolivia supply the largest quantities. Crude native bismuth contains 7 to 12 per cent. of the metal, the remainder being gangue. The following ores of bismuth are found in limited quantities:—Oxide **(bismuth ochre)**, carbonate **(bismuthite)**, sulphide **(bismuth glance)**, and **copper bismuth glance** ($3Cu_2S + Bi_2S_3$).

Winning of Bismuth.—Owing to the fact that bismuth is found native, the process of winning it often consists in liquating the metal from the gangue, this being rendered practicable by the low fusing point of the metal (268° C. = 514° F.).

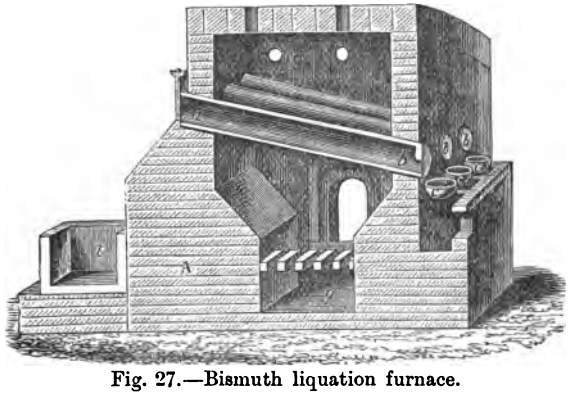


Fig. 27.—Bismuth liquation furnace.

A, Brickwork; *g*, grate; *a*, *b*, upper and lower ends of tubes; *c*, pots; *t*, water trough.

The liquation is effected in Saxony by breaking the picked ore into small pieces, and charging these into inclined iron tubes, *a*, set across the hearth of a long furnace (Fig. 27) with a grate, *g*, at one end. The lower ends of the tubes, *b*, which project through the wall of the furnace, have small openings to allow the liquated metal to flow into pots, *c*, where it is kept liquid until ready for casting into ingots. The residue left in the tubes consists of the earthy matter of the ore, containing silver, lead, tin, and arsenic. A Saxony ore containing cobalt and 10 to 30 per cent. Bi is liquated in crucibles instead of tubes, with the addition of reducing and desulphurising agents (carbon and iron) and an alkaline flux. The bismuth sinks to the bottom, and is covered by a layer of speiss,* consisting of sulphides and arsenides of

* See *Cobalt* and *Nickel*.

nickel, cobalt, and iron, above which is a layer of slag. The regulus of bismuth is re-melted before being cast.

A wet method of obtaining bismuth from oxidised ores, such as bismuth ochre and bismuthite, consists in dissolving the material in hydrochloric acid to saturation, and precipitating the metal by metallic iron. The black sludge thus produced is washed and fused in a crucible. When argentiferous lead contains bismuth, the last part of the cupellation slag contains the bismuth, which is less easily oxidisable than lead. This "black litharge" is extracted with hot hydrochloric acid, leaving insoluble chloride of lead (and of silver if present), and the solution is precipitated by the addition of much water, a bismuth oxychloride being thus obtained, which is reduced by fusion with charcoal and an alkaline flux.

The Refining of Bismuth.—Saxony bismuth may contain over 99 per cent. of bismuth, frequently indeed as much as 99·7 per cent., the chief impurities being As, Cu, and Ag. Cruder samples, from Peru and Australia, containing 93 and 94 per cent. Bi, 3 to 4 per cent. Sb, and some 2 per cent. of Cu, may be purified by liquation on an inclined iron plate.

When specially pure bismuth—*e.g.*, for medicinal purposes—is needed, modes of purification specially adapted for each impurity to be eliminated are employed. Thus, according to Matthey, arsenic may be removed by stirring the fused metal, kept at a temperature of 395° C. = 743° F. in contact with air, the whole of the arsenic being eliminated by volatilisation as oxide at 513° C. = 955° F. Antimony rises to the surface of fused bismuth as a film rich in antimony which can be skimmed off, the temperature most suitable for the operation being 350° C. = 662° F. The antimony oxidises during this process, and forms a glass consisting largely of oxides of antimony. Copper can be got rid of by fusing the metal and stirring in sodium sulphide, a slag containing copper and some bismuth being formed. The skimmings contain, on an average, about 10 per cent. of the bismuth treated, and are reworked. For the removal of gold and silver about 2 per cent. of zinc is added to the fused metal, as in the Parkes process for desilverising lead (p. 178). The skimmings are fused with borax for the recovery of the precious metals. Argentiferous bismuth may also be refined by pattinsonising (p. 177). When a metal approximately chemically pure is required, a wet process is probably most suitable, the bismuth being obtained as a basic salt which is reduced with pure reducing agents and fluxes. Bismuth containing 99·9 per cent. Bi can be thus obtained.

Properties and Uses of Bismuth.—Bismuth is a greyish-white metal of specific gravity 9·8, characterised by the ease with which it crystallises (in cubes often arranged in hollow pyramids, like NaCl). It melts at 268° C. = 514° F., and expands considerably on solidifying. It is used in thermo-

electric couples in conjunction with antimony, for making pharmaceutical preparations, and for lowering the fusing point of alloys, such as "fusible metals," melting below the boiling point of water—*e.g.*, *Wood's metal*, which consists of 4 parts of Bi, 2 parts of Pb, 1 part of Sn, and 1 part of Cd. Its oxide is also employed in the manufacture of glass for optical purposes.

NICKEL.

The most important ore of nickel is a recently discovered mineral consisting of magnetic iron pyrites (Fe_3S_4—pyrrhotite), containing nickel in place of iron to the extent of about 3 to 8 per cent.; this is associated with chalcopyrite (copper pyrites, $Cu_2S.Fe_2S_3$). This nickel ore is free from arsenic, and contains a trace of cobalt and platinum.* It is found at Sudbury in Canada deposited in diorite, a rock composed of hornblende and triclinic felspar.

Garnierite. — This is an hydrated silicate of nickel and magnesium, found in New Caledonia and the Ural mountains, of a composition corresponding approximately with the formula $NiMg(SiO_3)_2 3H_2O$. The proportion of nickel to magnesia is, however, usually lower than is indicated by this formula, and the ore is commonly associated with oxides of iron and siliceous gangue. The percentage of nickel ranges from 5 to 20 per cent., averaging about 7 per cent. Another ore, also found in New Caledonia, but of less importance than garnierite, contains cobalt and manganese in addition to nickel. Garnierite is remarkable for being almost the only nickel ore which is free from cobalt.

Arsenides, antimonides, and **sulphides** of nickel have been longer known as sources of the metal than have the two foregoing ores. These constitute the European ores, and occur principally in Saxony, Bohemia, and Scandinavia.

Kupfer-nickel (NiAs), specific gravity 7·4, **antimonial nickel** (NiSb), **nickel glance** ($Ni(AsS)_2$), **nickel blende** (NiS), and **nickeliferous iron pyrites** are examples of this class of ore.

Winning of Nickel.—Nickel, standing metallurgically between iron and copper, can be won by processes analogous with those proper to both the latter metals. Thus, sulphide ores may be run to a matte (although this cannot be self-reduced), and oxide ores directly reduced to crude metal. A similar relation is evident in the behaviour of nickel when treated by the wet methods of extraction, which resemble those for copper, although this process will not serve for the direct precipitation of nickel as metal, its similarity to iron preventing such easy reduction. The stability and volatility of nickel chloride ($NiCl_2$) and the existence of nickel carbonyl $Ni(CO)_4$ have led to suggestions for winning nickel directly by the volatilisation of the metal from

* As sperrylite, see p. 217.

the ore in the form of these compounds, but neither process has yet proved practicable.

Extraction of Nickel from the Sudbury Ores.—As examples of these ores the following analyses may be quoted:—

	1. Per cent.	2. Per cent.
Silica,	13·44	24·55
Iron,	39·02	35·18
Sulphur,	26·26	18·27
Copper,	4·31	1·43
Nickel,	5·57	3·74
Alumina,	4·49	8·02
Lime,	2·28	2·06

About 0·1 per cent. of cobalt occurs in these ores.

The ores are crushed and hand-picked into copper ore and nickel ore; the latter is roasted in heaps for several weeks until the sulphur is reduced to about 7 per cent. and the bulk of the iron oxidised. The ore is next put through a water-jacketted cupola in which the siliceous gangue is fluxed by the oxide of iron, alumina and lime, and the sulphides of copper, nickel, and iron run down to a matte of the following composition:—

	Per cent.
Copper,	20 to 25
Nickel,	18 to 23
Iron,	25 to 35
Sulphur,	20 to 30

The fused matte is tapped into a pot and the slag separated. The matte is next refined in a Bessemer converter similar to those used for copper mattes (see *Copper*, p. 163). During this part of the process the iron is oxidised* and fluxed, and a matte corresponding with "fine metal" (see *Copper*, p. 162) obtained, having the composition Cu 45, Ni 40, S 5 to 15 per cent. Owing to the fact that nickel sulphide stands between iron sulphide and copper sulphide in respect of the ease with which it is oxidised, care has to be taken in stopping the blow at the point when the iron is completely oxidised. As there is no definite indication when this point is reached, the success of the operation depends wholly on the judgment of the workman.

The Bessemer matte serves principally for the production of Ni and Cu alloys—*e.g.*, German silver—for which purpose the sulphur is removed by roasting and the substituted oxygen by reduction with charcoal, or other carbonaceous matter. The resulting alloy, consisting of 50 per cent. Cu and 49 per cent. Ni, is very similar to nickel in appearance, but has a lower melting point. For the production of pure nickel, the nickel is separated from the Bessemer matte in the form of oxide by roasting the matte, submitting it to a chlorinating roasting (see *Silver*), and

* The greater ease with which iron is oxidised and converted into silicate than is nickel, is utilised in this and similar separations.

extracting the copper chloride thus formed. The nickel oxide is ground and reduced, as described below.

Extraction of Nickel from New Caledonian Ore (Garnierite).—As the ore is a double silicate of nickel and magnesium, free from sulphur, an obvious method of treating it consists in reducing it with carbon, using limestone as a flux, in a blast furnace, thus obtaining a crude metal corresponding with cast iron. The composition of the "fonte" obtained in this manner is given below :—

	Per cent.
Nickel,	70·70
Iron,	22·00
Graphite,	1·78
Sulphur,	1·65
Aluminium,	1·37
Magnesium,	0·10
Oxygen and combined carbon,	1·88

The crude metal may then be converted into a sulphide matte in a manner similar to that about to be described.

This process, though simple in principle, has proved unsatisfactory in practice owing to the refractory character of the nickel and its slags, which are rich in magnesia. An improvement consists in winning the nickel as a sulphide matte by running down the ore with half its weight of gypsum or alkali waste and 20 per cent. of coke. The nickel is thus converted into sulphide and a portion of the iron fluxed as silicate. The resulting matte contains 50 to 55 per cent. Ni, 20 to 30 per cent. Fe, and 16 to 18 per cent. S. It is refined either in a Bessemer converter, or by roasting and fusion with sand to flux the iron as silicate, the nickel being obtained as sulphide. This is crushed, roasted to oxide, and reduced to metal in the manner described below. The ore is, however, now generally imported into Europe and worked by wet methods—*e.g.*, by dissolution in hydrochloric acid and precipitation of the nickel as oxide.

Extraction of Nickel from European Ores (Arsenides, Antimonides, and Sulphides).—The pyritic ores, containing some 2 per cent. Ni, 50 per cent. Fe, and 30 per cent. S, are roasted in heaps and fused for a coarse metal. In these processes iron is oxidised and fluxes the siliceous gangue. The resulting coarse metal contains about 5 per cent. Ni, 2 to 5 per cent. Cu, 30 per cent. S, and 60 per cent. Fe. It is roasted in heaps and smelted in small blast furnaces with quartz, to flux the oxide of iron produced by the roasting.

The amount of nickel in this regulus is about 50 per cent. and the copper 25 per cent., the remainder being iron and sulphur. A fusion for a fine metal in an oxidising furnace then follows, the remainder of the iron being thus oxidised and fluxed by added quartz. The fine metal contains 60 per cent. Ni, 30 per cent. Cu, 8 per cent. S, and 0·5 per cent. Fe. (In processes of

this type, especially as formerly practised, the main product was an alloy of Ni and Cu, the demand for nickel itself being but small.) In order to completely desulphurise the fine metal, it is ground and roasted "dead," the mixed oxides being subsequently reduced in crucibles with powdered charcoal. To obtain pure nickel from the roasted fine metal, advantage may be taken of the greater solubility of copper oxide than of nickel oxide in dilute sulphuric acid, the residue of nickel oxide left by this treatment being subsequently reduced (*v.i.*).

Arsenical nickel ores are worked to a speiss either in working argentiferous lead ores (see *Lead*, p. 176) or as a separate process, consisting of roasting in heaps and smelting with quartz in a blast furnace. The coarse speiss contains about Ni 45 per cent., Co 4 per cent., Cu 0·75 per cent., Fe 10 per cent., S 4 per cent., As 36 per cent. By melting this in a reverberatory furnace with a siliceous slag, the iron is fluxed and much arsenic oxidised and volatilised. The fluxing is continued until the blue tint of the slag indicates that the scorification of cobalt is beginning. The roasting is continued so long as it is possible to remove solidified oxides from the surface of the bath. The refined speiss contains 60 per cent. Ni, 3 per cent. Co, 1 per cent. Cu, and 36 per cent. As. It is ground to powder and roasted until it has acquired a bright green colour, being converted into nickel arsenate, $2NiO.As_2O_5$. By heating this to a very high temperature in a reducing atmosphere, the arsenic is volatilised and a portion of the nickel reduced to metal. This material still contains 1 to 2 per cent. As, which is removed by fusion with sodium nitrate and carbonate and subsequent washing with water, being thus dissolved as sodium arsenate. The nickel oxide is then reduced.

Much speiss is imported to Birmingham, where it is fused with lime and fluor spar, ground and roasted to free it from most of the arsenic. The subsequent treatment is designed for the recovery of the cobalt; the roasted speiss is dissolved in hydrochloric acid, the iron in the solution peroxidised by bleaching powder, and chalk is added; this precipitates both iron as basic carbonate and arsenic as ferric arsenate. The copper is thrown out by H_2S, the solution again peroxidised by bleaching powder, and lime added to neutralise the hydrochloric acid liberated by the precipitation of the copper. Cobalt peroxide is thus thrown down, it being more readily formed than the corresponding nickel compound. The nickel still in solution is precipitated as the normal oxide by milk of lime.

In the **reduction of nickel oxide**, obtained in any of the above processes, it is not generally economical to fuse the resulting metal, as its melting point is high (1,600° C. = 2,912 F.). It is, therefore, usual to make the oxide into a paste with charcoal and carbonaceous material, such as flour or oil, and compress it

into slabs which are cut into small cubes, the shape of which is retained by the metal when reduced. With modern regenerative furnaces, however, nickel can be completely fused and obtained as cast metal. Commercial nickel is never pure, but contains, like iron, carbon and silicon. The following are analyses of cast nickel :—

	I. Per cent.	II. Per cent.
Carbon,	1·10	...
Silicon,	0·13	0·19
Iron,	0·10	0·30
Sulphur,	0·26	0·07
Nickel,	98·39	98·68
Copper,	...	0·76

Properties and Uses of Nickel.—Nickel has a specific gravity of 8·8 ; fuses at 1,600° C. = 2,912° F., and ranks below iron in electrical conductivity. Nickel greatly resembles iron, differing from it mainly in its stability in air and water. It stands next to manganese in hardness, it is magnetic at ordinary temperatures, but not at temperatures above 250° C. = 482° F. Cast nickel is not very malleable, but may be improved in this respect by fusion with a powerful reducing metal—*e.g.*, magnesium, aluminium, or manganese—their action recalling that of phosphorus upon over-refined copper, p. 161. Nickel is principally used for alloying with copper to produce nearly white alloys of the German silver class, its whitening effect being remarkable.*

German Silver varies much in composition, its price and value increasing with the proportion of nickel. It may be regarded as a nickeliferous brass, and ranges between the limits, copper 50 to 70 per cent., zinc 20 to 40 per cent., and nickel 15 to 25 per cent. **Platinoid**, used for electrical resistances, is a German silver containing 1 to 2 per cent. of tungsten. **Coinage nickel** consists of copper 75 per cent. and nickel 25 per cent., and is white in spite of the large proportion of copper. Lately, nickel has been largely used for the manufacture of nickel steel (*q.v.*). The resistance of nickel to rust has led to its use for plating of other metals by electro-deposition. Its resistance to fused alkalies renders it applicable for laboratory vessels.

COBALT.

This metal so nearly resembles nickel that the metallurgy of the two may be conveniently taken together. It is mostly a bye-product in nickel works, being separated as already described after the removal of the remaining constituents of the ore. Definite cobalt ores are **smaltine** or **speiss cobalt (tin white cobalt)**, $CoAs_2$, **cobalt glance**, CoAsS, **cobalt bloom**, $Co_3As_2O_8$

* An alloy containing about 66 per cent. Ni and 33 per cent. Cu, which greatly resembles nickel in appearance, is sometimes ignorantly or wittingly offered in its place. It may be detected by the fact that it is not attracted by a magnet.

(the normal arsenate), **black earthy cobalt,** consisting of hydrated oxides of cobalt and manganese and **cobalt pyrites.** The metal itself is more strongly magnetic than nickel; it has a specific gravity of 8·9 and a melting point of 1,500° C. = 2,732° F. In the metallic state it is chiefly used for plating, yielding a better coating than nickel. Its main use, however, is in the production of pigments (*q.v.*, Vol. II.), for which purpose the peroxide separated in the systematic extraction of nickel already described is worked up. Cobalt ores are worked on the same general lines as those of nickel, but recently a process depending on the stability of cobalt chloride has been utilised. The arsenides and sulphides are roasted, ground, mixed with ferric chloride, made into a paste with ferrous chloride, moulded, dried, and calcined. A chlorinating reaction typified by the following equation occurs:—

$$CoO + FeCl_2 = CoCl_2 + FeO.$$

The cobalt chloride is leached out and worked up by the wet method described above for the separation of nickel and cobalt.

MERCURY.

Mercury is found **native,** both alone and as an amalgam with silver. Native mercury may occur collected in cavities, or in a finely-divided state distributed through cinnabar. Its chief source, however, is its sulphide (HgS), found in the form of **cinnabar,** which is won in large quantities in Spain, Austria, and California. This is a heavy crystalline mineral (specific gravity 8·2), red or brown in colour. It is sometimes found in a black amorphous form **(metacinnabar),** the two varieties corresponding with the red and black form of HgS prepared in the wet way.

Methods of Winning Mercury from Cinnabar.—Owing to the ease with which mercuric oxide is decomposed, mere roasting of cinnabar yields SO_2 and Hg, not HgO. The removal of sulphur may be affected by other reagents than oxygen—*e.g.*, lime and iron. Two types of process for winning mercury from cinnabar may therefore be distinguished.

1. **Removal of the Sulphur by Roasting in Air.**—The crudest method of effecting this consists in roasting the ore in heaps, enclosed by brickwork, and provided with flues similar to those sometimes used for coking coal (see *Coke*, Vol. II.). The mercury volatilised from the lower portion of the heap is condensed in the upper layer, from which it may be washed on a sieve, the ore-dust and mercury being washed through, whilst the coarser portion is used for the lower layer of the heap next to be roasted. The process is adapted for treatment of copper ores (*fahlerz*) which contain from 0·5 to 17 per cent. Hg, and are afterwards

to be worked for copper. In better processes the roasting is carried out in an enclosed furnace, and the mercury vapour condensed from the flue gases by passage through a series of receivers or chambers. Thus at Idria, by the old process, chambers like those shown in Fig. 28 serve for the condensation of the vapour expelled from the ore (containing 10 to 12 per cent. Hg), which is roasted on the shelves, *a*, *b*, *c*, disposed over the grate, A. The final chambers, D, are provided with water cascades to complete the condensation. The mercury collects in an underground channel. In the more modern Idrian furnace a continuous distillation is effected in a cylindrical kiln charged at the top through a hopper, and connected with six condensing chambers externally cooled by water. The spent ore is raked out through bars at the bottom of the furnace, and fresh charges introduced by the hopper. When once started, the reaction $HgS + O_2 = Hg + SO_2$ continues, as it is exothermic, but the

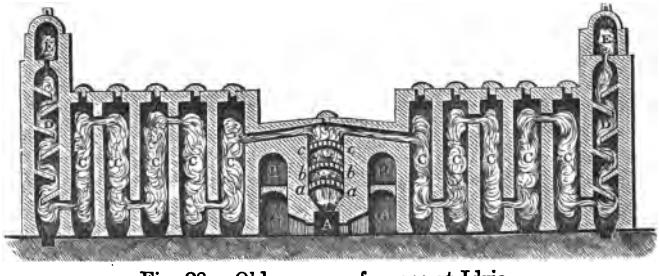


Fig. 28.—Old mercury furnace at Idria.

a, *b*, *c*, Shelves; A, grate; C, condensing chambers; D, water chambers; E, aperture for escape of gases.

heating effect is supplemented by the combustion of about 4 per cent. of charcoal added to the ore charged. For poor ores, which contain so much gangue that the combustion of their mercuric sulphide is insufficient to maintain the temperature of reaction, heating from some source other than the combustion of the ore is requisite. The direct admixture of fuel is not advisable, as sufficient oxygen for the combustion both of it and of the HgS would be difficult to supply, and HgS would be sublimed unchanged. This necessitates the use of a reverberatory furnace, by which means an ample supply of air, together with the requisite heat, can be obtained. The plant for winning mercury from poor ores (1 per cent. Hg) by this method includes, therefore, a reverberatory furnace connected with a condensing chamber, which is coupled in its turn with a second chamber by means of a wide iron pipe, cooled by an external water spray. The necessity for the use of air as an oxidising agent causes the mercury vapour to be diluted with much nitrogen as well as

SO_2, and, therefore, to be difficult to condense. When working poor ores, the dilution is increased by the gases of the external furnace, thereby making the use of the comparatively elaborate condensing arrangements described above inevitable. In any case, considerable loss of mercury must occur, as at the temperature of the exit gases mercury possesses an appreciable vapour tension. There is also a loss of mercury in the form of mist, which is comparable with that given when many soluble vapours are passed through water—*e.g.*, NH_4Cl and SO_3.

Another system of condensation is that practised at Almaden in Spain. The mercury vapour and spent gases are passed through a series of **aludels** (Fig. 29), which are clay, pear-shaped vessels fitting one into the other. The line of aludels slopes first down from the kiln and then up the flue, thus

Fig. 29.—Mercury aludels.

a gutter being placed at the lowest point of the depression, so that the mercury condensed in either half of the series is received in a common channel. The members on the side of the series descending from the kiln, which receives the bulk of the mercury distilled, are provided with holes at the lower part which are stopped with sand, so that the mercury may filter through, and thus be removed, immediately on its condensation, from the current of hot gases passing through the aludels. The filtered mercury flows down a plane to the central channel. This system of condensation has the disadvantage of involving the making of numerous joints (often leaky) in connecting the aludels.

At New Almaden, in California, coarse ore furnaces for continuous working consist of an hexagonal base, at three alternate sides of which are the hearths. The ore chamber above the hearths is cylindrical. The ore, mixed with about 2 per cent. of coke, is charged in through a hopper at the top; and when it is at a cherry-red heat, the lower, spent portion is raked out into the ashpit, and fresh ore charged. The content of mercury varies from 6 to 8 per cent. Condensation is sometimes effected in receivers of thin glass sheet set in wooden frames, this material being preferable to iron or earthenware, at temperatures below the boiling point of water, as it is not attacked by the condensed sulphurous and sulphuric acid. "Fines" are treated, also continuously, in a vertical furnace which is fitted with inclined shelves (Fig. 30).

The fines are delivered from a hopper on each side of the middle partition of the furnace and fall from shelf to shelf, turning over during their progress, so that every portion is

exposed to the action of the hot air ascending from the hearths at the base of the kiln.

In any of these processes mercurial soot **(stupp)** condenses in the chambers. It contains about 20 per cent. Hg, both as metal and as sulphate, &c. It is made into briquettes with lime (to decompose the sulphate) and re-worked.

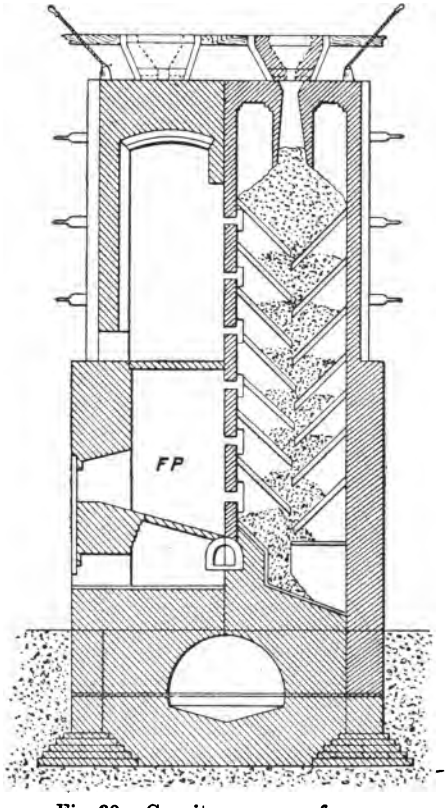


Fig. 30.—Granitza mercury furnace.

2. **Removal of the Sulphur by Lime or Iron.** — The winning of mercury from cinnabar by distillation with iron takes place according to the equation—

$$HgS + Fe = Hg + FeS.$$

When lime is used to remove the sulphur the reaction is stated to be

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

In practice, the ore is mixed with iron or lime and heated in small bottle-shaped retorts, a number of which is set horizontally in a long gallery furnace. The mercury distils into receivers containing water, the condensation taking place much more readily than when the mercury vapour is diluted with inert gases, as in the case of the roasting process already described. Larger charges than can be distilled from these iron bottles are dealt with in iron retorts similar in shape to those used in the manufacture of coal gas (*q.v.*, Vol. II.). In the course of the distillation, finely-divided mercury and undecomposed sulphide come over with the main product, and are redistilled with more lime.

The purification of crude mercury is merely a process of filtration, the metal being forced through wash-leather.

Properties and Uses of Mercury.—The specific gravity of mercury at 0° C., compared with water at 4° C. = 39·1° F., is 13·546 (*Volkmann*). It solidifies at −39° C. = −38° F., and boils at 357° C. = 675° F. The fact that its coefficient of expansion is remarkably uniform fits it for the construction of thermometers, and its high specific gravity for that of barometers. It is used for the extraction of gold and silver by amalgamation, and for the manufacture of looking glasses. For this purpose a sheet of tin foil is placed on a marble slab carefully levelled; a thin layer of mercury is then spread over the whole surface, the glass to be "silvered" is slid on to the prepared table and weighted, being left thus for some weeks. During the time of silvering the table is inclined to allow the surplus mercury to drain away.*

SILVER.

SILVER ORES.—Owing to the low heat of combination of silver with oxygen it is not surprising that a good deal of the metal occurs **native**, although it is frequently alloyed with other metals, such as gold, copper, and, in rarer instances, mercury. It is also sometimes associated with antimony as an antimonide, varying in composition from Ag_2Sb to Ag_6Sb. Cubic and octahedral crystals of silver, both massive and in dendritic forms, occur in many localities, but are especially abundant in Norway and Peru. Native silver may contain 90 to 99·8 per cent. Ag.

Silver sulphide (Ag_2S) occurs both alone (*argentite*) and together with antimony sulphide in the two forms—**brittle silver ore**, $5Ag_2S.Sb_2S_3$, and **ruby silver ore**, $3Ag_2S.Sb_2S_3$; **light red silver ore** corresponds with the latter, arsenic replacing antimony, and **polybasite** may be regarded as a mixture of the two, together with sulphide of copper.

Silver telluride, Ag_2Te, analogous with the sulphide, is found, as is also **silver selenide**.

Silver chloride (*horn silver*), AgCl, is found in considerable

* Looking glasses are now truly silvered with Ag, *cf.* p. 209.

quantities in Chili and Peru, both massive and as scattered cubical crystals. It receives its metallurgical name from its appearance and texture. **Silver bromide** and **iodide** sometimes occur associated with the chloride.

Other Metallic Ores containing Silver.—As has been already stated, certain ores, notably galena and copper pyrites, contain small quantities of silver, and are worked for the recovery of that metal as an incident in the process of winning the main metal (*e.g.*, lead or copper) in the ore. The preliminary stages of the extraction of silver from such ores—*i.e.*, its concentration before recovery—have been described in the chapters dealing with the ores themselves. The largest portion of the world's supply of silver comes from the United States, Mexico, and South America. Australia (notably from Broken Hill) contributes a large quota.

WINNING OF SILVER FROM ITS ORES.—1. **General Principles.**—Silver is one of the most easily reducible metals, owing to the circumstance that its oxide is split up at a red heat, as indeed is illustrated by the fact that it may be reduced in the laboratory from a salt, such as silver chloride, by heating with an alkaline flux—*e.g.*, sodium carbonate—without a reducing agent, the reaction taking place on the following lines :—

$$2AgCl + Na_2CO_3 = Ag_2O + CO_2 + 2NaCl.$$
$$Ag_2O = 2Ag + O.$$

On a large scale, ores are seldom rich enough in silver or sufficiently free from other metals to make such direct extraction a practicable method. Silver has, however, a special tendency to dissolve in other metals and in metallic sulphides, hence it can be conveniently concentrated by fusion of the ore with a flux, and, if necessary, some other ore to provide the solvent metal or sulphide. Examples of this, when the ore is particularly poor, have already been given under lead and copper smelting (*q.v.*). In the case of lead the silver concentrated in this way is extracted by again taking advantage of the fact that silver oxide does not exist at a red heat, so that the lead can be oxidised and removed, leaving the silver as metal. In the case of the copper sulphide the process depends on the circumstance that silver shows its similarity to the alkali metals by the stability of its sulphate (Ag_2SO_4), which is formed on roasting the matte, and is not decomposed by a temperature sufficient to decompose the copper sulphate which is simultaneously formed. Another instance of the collection of silver in a solvent is afforded by the use of mercury at the ordinary temperature, corresponding with that of lead at a high temperature. In this case, as no decomposition of a silver salt by heat can be employed, some other means of obtaining the silver as metal is necessary. The mercury will subserve this purpose as well as act as a collecting agent.

The other general principle applied in methods of silver extraction is the ease with which silver chloride can be formed by roasting silver ores with salt, the stability of the chloride thus produced and its solubility in solutions of other chlorides or of thiosulphates (hyposulphites). A precipitation of the dissolved silver as metal or as sulphide serves for its recovery when thus extracted.

2. **Dry Processes for Winning Silver.**—(*a*) **Extraction with Lead as a Solvent.**—The production of ordinary argentiferous lead (from galena) has been already described (see *Lead*). When the silver is present in sufficient quantity to cause the ore to be classed as a silver ore, the reduction is effected in blast furnaces to the exclusion of those of the reverberatory type. With poor ores the lead is sometimes collected in a pyrites matte

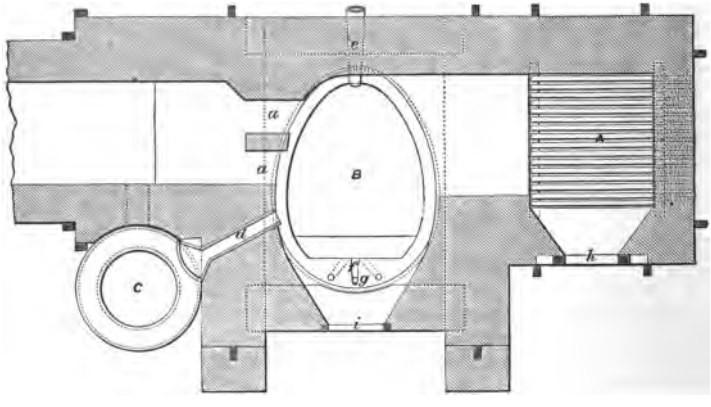


Fig. 31.—Section of cupellation hearth.
A, Grate; B, test; *e*, twyer; *a*, *a*, flues; C, iron pot; *f*, channel; *g*, vent: *i*, door.

by adding this mineral to the furnace charge; the resulting matte is roasted in heaps, and fused with richer ores whereby an additional proportion of silver is extracted; the metal may be now transferred to lead by running the matte into a bath of metallic lead; the silver sulphide in the matte is thus reduced and the silver retained by the lead. Argentiferous lead containing upwards of 1 per cent. Ag (30 ozs. per ton) can be cupelled directly, but poorer metal must be enriched by one of the processes of concentration (Parkes or Pattinson), described under *Lead*. When concentration is adopted, much richer leads are cupelled—*e.g.*, such as contain 300 ozs. of silver per ton. The works process of cupellation combines the features of the laboratory processes of scorification and cupellation, the lead being oxidised and the oxide (l) allowed to flow off the remaining

metal, as in scorification, and (2) absorbed by the material of the hearth, as in cupellation.

A horizontal section of the cupellation hearth is shown in Fig. 31. The fire grate, A, is placed at one end of a long flue across which is the egg-shaped frame, or "test," B. This frame is filled with bone ash and serves to contain the lead to be treated. The twyer, *e*, supplies a blast of air which plays upon the surface of the lead. The flame of the fire passes across the test, the products of combustion passing away by the flues, *a a*. From 4 to 5 cwts. of the lead are melted in an iron pot, C, and run through the gutter, *d*, on to the test. When its surface becomes covered with fused litharge the blast is turned on, and the melted oxide is driven in waves over the surface of the lead, escaping through the channel, *f*, and the vent, *g*. The progress of the operation is watched through the door, *i*, and fresh lead is charged in from time to time until the enriched alloy contains about 8 per cent. of silver. It is not profitable to concentrate this further on the same test, inasmuch as a continually increasing proportion of silver passes into the litharge, and is troublesome to recover from the whole quantity. At this stage, therefore, the metal is tapped by making a hole in the floor of the test. It is transferred to a new test where the process is continued until the surface of the metal becomes bright, indicating that no further oxidation is taking place and that silver remains. The silver is either tapped or allowed to solidify on the test. This silver contains from 99·7 to 99·8 per cent. Ag, and is refined by again heating it on a cupel, the impurities (save gold)—*e.g.*, Cu, Pb, Bi—being oxidised and absorbed. The litharge, especially the last portions rich in silver, is reduced, concentrated by pattinsonising and re-cupelled. The cupels are broken up and smelted for the recovery of lead and silver.

(*b*) **Extraction with Copper Matte as a Solvent.** — In the case of this process the silver is a bye-product, the copper being the metal primarily to be won. As already described under *Copper* (p. 163), a matte containing cuprous sulphide and some iron sulphide and silver sulphide (0·5 per cent. Ag) is roasted, the iron and copper being converted into oxides and the silver into sulphate (this salt being very stable, as already mentioned). To avoid decomposing silver sulphate the roasting must be stopped before a sample ceases to give a blue solution (presence of $CuSO_4$). The silver sulphate is leached out with water containing a little sulphuric acid (to prevent the formation of basic salts) and the silver precipitated by copper, the copper being recovered by means of iron.

The precipitated silver is washed with dilute sulphuric acid to remove remaining basic copper salts, pressed into blocks, fused and refined by an oxidising roasting (sometimes with the addition of saltpetre) in a reverberatory furnace.

3. Wet Processes for Winning Silver. — (A) Extraction of Silver by the Use of Mercury for Collecting and Dissolving it (Amalgamation Processes).—In amalgamation processes reduction of the silver in the ore to the metallic state—a necessary preliminary—is most readily effected when the silver is in the form of chloride, on which account the ores containing sulphides, &c., are either roasted with salt,* or, if fuel be scarce, treated during the process with copper chloride (in the form of a mixture of salt and copper sulphate) which is capable of reaction with silver sulphide at a sub-tropical temperature.

1. *Amalgamation Process with Iron as a Reducing Agent.*—(*a*) *Barrel Process.*—This method, which is now nearly obsolete, is a typical amalgamation method and may be briefly described.

The crushed ore is roasted with salt to convert the silver into chloride, and charged, together with scrap iron, into rotating barrels with enough water to make a thin paste. After some hours rotation, mercury and sometimes a little copper sulphate are added and rotation is continued for a longer period. The barrels are then filled with water, and the mercury, holding silver in solution, run off from the bottom. The silver amalgam is distilled in iron retorts resembling gas retorts (sometimes under reduced pressure) and the silver recovered.

(*b*) *Pan Amalgamation* or *Washoe Process.*—In this method the finely stamped ore is graded by settling, it being essential that the subdivision shall be fine. It is then ground in an iron pan with iron mullers, with mercury and sufficient water, the pan being heated to about 85° C. = 185° F. by steam. The iron of the pan and mullers, in conjunction with the mercury, reduces the silver to metal and an amalgam is formed. It is found that even sulphide ores can be worked in this way, a probable reason being that the ore is in a fine state of division and the temperature is high. Sometimes chlorinating agents — *e.g.*, copper chloride—are added to the charge, their action being similar to that described under the Mexican process (*v.i.*) The contents of the pan is washed into a separator. This is a tub the bottom of which slopes from the centre to the circumference and is traversed by a number of rakes. There being enough water in the tub to allow of a fractional subsidence, the mercury and amalgam collect on the bottom and are run off, strained, and distilled in the usual way.

2. *Amalgamation Process with Mercury as a Reducing Agent (Mexican Process).*—Crushed ores are ground to powder in a primitive edge-runner mill, together with a little mercury if free gold or silver be present. The ground ore, in the form of a mud, is spread on a floor and trodden by mules, with about

* In such chlorinating roastings the sulphide is first converted into a sulphate which then reacts with the sodium chloride, giving sodium sulphate and a chloride of the metal under treatment.

4 per cent. of common salt. Mercury and "magistral" (*i.e.*, roasted copper pyrites, consisting chiefly of $CuSO_4$, $FeSO_4$, CuO, and Fe_2O_3) are added, the former to the extent of about six times the silver content of the ore. After a further intermixture a hot solution of copper sulphate, in proportion varying with the amount of sulphur and arsenic in the ore, is run on to the heap. Copper precipitate may be advantageously added, probably because its reducing effect on the silver supplements that of the mercury. The chemistry of this and like processes has not been thoroughly worked out, but the chief reactions occurring appear to be (*a*) the reaction of copper sulphate with sodium chloride, giving cupric chloride and sodium sulphate; (*b*) that of cupric chloride on silver sulphide, giving cupric sulphide and silver chloride, the latter then dissolving in the solution of sodium chloride; (*c*) the reduction of silver chloride to silver by mercury, aided by copper, with the formation of mercurous chloride and cuprous chloride; and (*d*) the formation of silver amalgam by the interaction of silver and mercury. When these changes are complete, more mercury is added to the charge and the whole stirred with water in a tank; the silver amalgam settles, is run off, and filtered through canvas to separate the excess of mercury from the semi-solid amalgam. The amalgam is distilled, frequently by the simple process of heating it in a series of vertically disposed trays covered by an iron bell standing in water; the upper part of the bell is encased in a furnace and the mercury condenses in the water reservoir.

(B) **Extraction of Silver by Dissolution and Precipitation.**—In the preceding processes, both dry and wet, concentration by collection of the silver in a solvent (lead and mercury) has only been possible after reduction to the metallic state. In like manner, in the processes about to be described, the silver has to be converted into chloride before its dissolution and extraction. Only two solvents are commonly employed—viz., a strong solution of sodium chloride and one of sodium or calcium thiosulphate.

(*a*) *Extraction with Sodium Chloride and Precipitation by Copper* (*Augustin's Process*).—Both ores and copper mattes are first roasted alone, by which process the bulk of the sulphides is converted into oxides, but owing to the stability of silver sulphate (*v.s.*), most of the silver sulphide is converted into this salt. The roasted material thus contains most of the copper (and iron) as oxides, but a portion as basic sulphate; most of the silver is as sulphate, but a part still as sulphide. On re-roasting with salt, the oxides are unattacked, whilst the sulphates of copper and silver are converted into chlorides by double decomposition. The residual silver sulphide, when roasted in the presence of sodium chloride, undergoes the change characteristic of a chlorinating roasting, forming, first, sulphate, and then, by

double decomposition, silver chloride and sodium sulphate. In the Ziervogel process (see *Copper*, p. 163), the whole of the silver sulphide must be converted into sulphate in order to be extractible, necessitating very careful roasting, whereas in the present case, residual silver sulphide from the first roasting is not lost because afterwards transformed into chloride. The final product, whether from matte or ore, consists of copper oxide (and ferric oxide), silver chloride, and sodium sulphate. From this the silver chloride is extracted by leaching with a hot, strong solution of common salt, in which it is fairly soluble.* The brine containing silver chloride is filtered through a layer of cement copper (see p. 165), the silver being precipitated and the copper going into solution as chloride. The cement silver is washed with hydrochloric acid and refined in the usual way.

The principles of this process have been applied to the treatment of argentiferous copper bottoms (now generally refined, with recovery of silver, by electrolysis—see p. 167), which are granulated, roasted to oxide, ground and roasted again with ferrous sulphate, which acts in the same way as the sulphate resulting from the roasting of a matte (detailed above). The product is leached with water as in the Ziervogel process (p. 163), and the residue, containing silver as sulphide, is roasted with salt and extracted in the manner proper to the Augustin process.

The recovery of silver from burnt pyrites by the *Claudet process* resembles the Augustin as far as the obtainment of a solution of silver chloride in sodium chloride is concerned, but the silver is separated by precipitation with an iodide, the silver iodide being collected and reduced with zinc, yielding the silver. The zinc iodide thus formed is used for precipitating a fresh portion of the chloride solution.

(*b*) *Extraction with a Hyposulphite and Precipitation as Sulphide* (*Patera's Process*).—The preliminary operations do not differ in principle from those already mentioned as preceding extraction with sodium chloride. Inasmuch as in this process the solution of silver chloride is to be treated with sodium sulphide (*v.i.*), it is advantageous to wash the product of the chlorinating roasting with water, in order to remove the chlorides of copper, zinc, iron, &c., which would otherwise be precipitated as sulphides, together with the silver sulphide. The residues from this washing are treated with a cold solution of sodium thiosulphate (or calcium thiosulphate, as in the *Kiss process*), the silver chloride being thus brought into solution. Sodium sulphide is added to the liquor until no further precipitation takes place, and the silver sulphide is roasted in muffles, any silver sulphide which is not thus decomposed being reduced by iron in crucibles (see *Reduction of galena by iron*, p. 175). When a solution of

* 100 parts of water saturated with sodium chloride dissolve 0·4 part of silver chloride at 100° C. = 212° F.

a double hyposulphite of sodium and copper (*Russell process*) is used, silver sulphide is said to be attacked, the silver being dissolved as the double hyposulphite of sodium and silver, and the copper precipitated as sulphide. The tailings from the lixiviation of a chlorinating roasting, containing unattacked silver sulphide, may be treated by this method.

The refining of silver is, as has been already stated, usually performed by roasting, supplemented by the action of oxidising fluxes—*e.g.*, saltpetre. An electrolytic method consists in casting the crude silver into plates which are made the anodes of a cell containing a 1 per cent. solution of nitric acid, the cathodes being thin silver plates. The anodes are enclosed in muslin bags which retain gold, platinum, and lead (the last as PbO_2), while silver and copper are dissolved, the former alone being precipitated on the cathodes.

Properties and Uses of Silver.—Silver has a specific gravity of 10·53, and a fusing point of 960° C. = 1,760° F. It is the best known conductor of heat and electricity. It is characterised by its stability in air free from sulphureous gases. For use in coinage and ornaments it is alloyed with copper. Thus, English sterling silver contains 92·5 per cent. Ag and 7·5 per cent. Cu. In the pure state silver is largely used for silver-plating, being deposited electrolytically from the double cyanide of silver and potassium. An alloy of silver and cadmium containing 10 per cent. or more of the latter metal, has lately been deposited electrolytically, and is less easily tarnished than pure silver. On account of the fact that silver can be deposited as a brilliant adherent film on glass, mirrors made with an amalgam of tin and mercury (see *Mercury*, p. 202) have been largely replaced by those prepared by allowing a solution of ammonio-tartrate of silver to deposit the metal on a clean glass surface, the reduction taking place when the solution is warmed.

GOLD.

Sources of Gold.—Gold is nearly always found native, alloyed with more or less silver. It occurs massive as nuggets, weighing from a fraction of an ounce to many pounds, and in veins distributed through quartz, generally associated with sulphide minerals—*e.g.*, pyrites and galena. In places where such veins have undergone a process of weathering, finely-divided alluvial gold is found in the beds of rivers now flowing or of ancient date. For the most part these gravelly deposits are loose in texture and easily disintegrated by water, but are sometimes found agglomerated in masses which have the appearance of bed-rock. In the above cases the true gangue is of a siliceous character, and the gold is comparatively easy to extract. There is, however, a considerable quantity of gold the gangue of which

consists of pyrites or galena with which the gold is so intimately associated as to have given rise to the opinion that it also is as sulphide. This does not appear to be the case, but tellurides of gold and silver are known. Gold is also a bye-product of the winning of other metals, notably silver, copper, and lead. The chief gold-producing countries are Australia, America (California), and Russia. The composition of native gold falls between the limits gold 64·77 to 99·2 per cent., silver 35·23 to 0·43 per cent., iron and other minerals up to 0·28 per cent.

Winning of Gold.—The bulk of the world's production of gold is obtained by comparatively simple processes, depending (*a*) upon the high specific gravity of the metal (19·32 when pure), and (*b*) upon the ease with which it is taken up by mercury. The washing and amalgamation of gold are mechanical processes, which will be dealt with here to illustrate typical methods for the concentration of ores generally by mechanical means. Such processes for winning gold as depend upon strictly chemical principles will be described later.

Concentration of Gold and Other Ores.—The fundamental principle underlying the mechanical concentration of gold ores is that when two particles of identical shape and equal volume but different weight are allowed to fall through a resistant medium, that which has the greater weight will fall faster than the other. It follows from this that the difference in specific gravity of two substances is an index of the ease with which they may be separated in this manner, provided the conditions of identity of shape and volume be maintained. But by increasing the size of the particle of lower specific gravity it will eventually fall as fast as that of the higher specific gravity, because the surface it exposes to the resistance of the medium is smaller relative to the impelling force (its weight). Also by altering the shape of the particle of lower specific gravity, so that it presents a smaller surface for a given volume than does the particle of higher specific gravity, a similar compensating effect will be obtained. Thus it is, that, though in ideal concentration the particles will be of identical size and shape and of different specific gravities, yet, in practice, imperfection of sizing and irregularity of shape necessitate large differences in specific gravity to compensate for these disturbing factors. The great difference in the specific gravity of gold (19·3) (native gold containing silver may have a specific gravity of 17 or less) and siliceous gangue (2·7) leaves a larger margin for providing this compensation than is available in most other cases.

Winning Alluvial Gold.—For a long time the mere washing of auriferous sands in pans where the necessary suspension was attained by hand-shaking, sufficed for winning gold. As no sizing was attempted, only a crude separation was thus possible. The "cradle," which is an inclined trough set on rockers, consti-

tutes a development of the pan.* It is plain that the process of permitting particles which are to be separated, to fall through a resistant medium, can be replaced by the plan of causing the medium to flow over the particles in a thin layer. An additional cause for separation here occurs—viz., the difference of velocity of the upper layer of a thin stream of water and the lower layer in contact with the channel through which it flows. This difference of velocity will allow of a still larger deviation from identity of size and shape, because the larger particles will stick up into the upper layer of the stream, and their upper parts will be exposed to its full force, so that they will tend to be carried on in spite of their size.

This principle is applied by washing the crushed ore or auriferous sand down an inclined plane with a thin stream of water. The separation is aided by rendering the floor of the channel rugose. Thus, the inclined channel is sometimes covered with a blanket or by "riffles"—*i.e.*, strips of wood dividing it into chequer work. When working auriferous gravel on a large scale, the method adopted is to direct a powerful jet of water on to the slope, the surface soil of which consists of the gold-bearing material, the process being termed "hydraulic mining." The debris is conveyed down a long sluice consisting of a series of wooden troughs set at a gradient of about 8 to 18 inches in 12 feet.

The bottom of the troughs is covered with riffles, in which the gold collects. The collection of the gold is aided by putting mercury in among the riffles. Methods of catching gold by means of mercury may be combined with all ordinary washing processes.

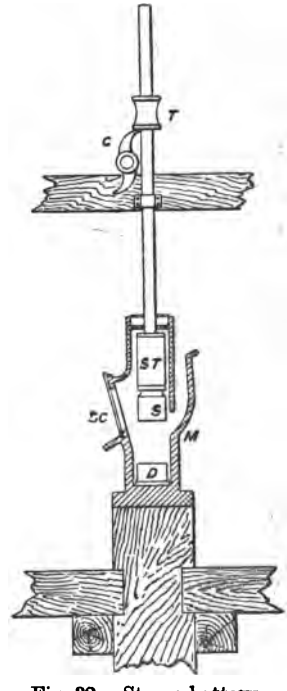


Fig. 32.—Stamp battery.

T, tappet; C, cam; ST, stamp; S, stamp head; D, shoe; M, mortar; SC, screen.

Winning Gold from the "Ore."—By "ore" is here meant any rock bearing gold, hard enough to require comminution by other means than mere washing. The chief processes requisite are:—

1. **Comminution.**—The ore is first put through a stone-breaker and then pounded in a stamp mill (Fig. 32). This consists of a

* In this case a rough sizing of the gold-bearing gravel by means of a riddle at the head of the cradle is generally adopted.

series of vertical pestles of great weight and shod with iron, alternately raised and allowed to fall by a shaft and cam, C, operating a tappet, T. The stamp, ST, with its head, S, strikes upon an iron block or shoe, D, in the mortar, M, into which the ore is fed. The mortar is covered and is provided with a hopper on one side for receiving the broken ore, and a rectangular opening opposite to this in which a screen, SC, to retain coarse fragments, is fitted. Most of the crushing is generally done dry and a stream of water is then let in, the motion of the stamps being continued. The crushed rock is thus churned with the water into a thin mud (*slimes* or *pulp*), the gold, if in large particles, sinking to the bottom of the mortar and being collected by mercury in the channel surrounding the block, D. The finer gold is splashed up and either flows through the screen with the slimes, or adheres to amalgamated copper plates which line the sides of the mortar.

2. **Amalgamation.**—That part of the gold which is not caught in the stamps is collected by concentration and amalgamation in the following manner:—In passing into the sluices the slimes first traverse amalgamated copper plates where much of the gold is retained, a further portion being caught by the blankets with which the sluice is lined, from which it is afterwards washed and collected in mercury by the aid of an amalgamating pan. After flowing through the sluices, the main slimes, together with those from the amalgamating pan, pass into some form of "rubber," in which they are triturated between iron surfaces in order to brighten the surface of the particles of gold, and thus enable them to be amalgamated, such amalgamation being often performed in the rubber, which is fitted with amalgamated copper plates.

3. **Concentration Proper.**—It will be noted that during the passage through the sluices and over the copper plates concentration as well as amalgamation takes place. A certain amount of finely-divided gold will, however, escape with the slimes from the rubbers, and this may be further concentrated in a systematic manner. The process of concentration is carried out by first sizing the material in "pointed boxes" having a V-shaped bottom in which there is a slit to permit of the passage of those grains which are of such a size and specific gravity as to sink. By using a series of such boxes of increasing cross-section the flow of water bearing the slimes will at first be too rapid to allow of any but the largest equal-falling grains to reach the bottom, become less rapid as it proceeds, and depositing successive fractions of decreasing size. The sized sands are then concentrated in sluices as before. Further concentration is effected in inclined rockers, buddles,* and tossing tubs.†

* The buddle is generally a round box with a coned bottom, sloping towards the circumference, over which brushes, set on radial arms, are carried. † Circular vessels provided with rotating agitators.

In modern practice a Frue vanner serves for concentrating the slimes. This consists essentially of an endless sloping rubber belt carrying a stream of water which flows in the opposite direction to that in which the belt is moved. The separating effect of the stream is here aided by the opposite motion of the belt, which also receives an oscillatory movement that favours segregation. The first-falling particles are thus collected at one end of the machine whilst the remainder flows off at the other end.

It will be seen that during these treatments a large proportion of the gold has been collected in mercury in the stamps and sluices, and another portion as **concentrates** (associated with pyrites). The gold amalgam is collected and distilled in the manner already described for silver (p. 206). Before leaving the subject of amalgamation it may be said that the cleanliness of the mercury is essential for its proper utilisation. As it tends to become foul by use it is "quickened" by stirring it with a solution of potassium cyanide or dilute acid, but is best restored to purity by distillation. Mercury containing a small quantity of sodium is said to be efficacious in keeping the bulk of the mercury active as a solvent. The concentrates (*v.s.*) are roasted to remove sulphur, and are either amalgamated or more usually chlorinated (*v.i.*) for the recovery of the gold which they contain.

Winning of Gold by Chemical Processes.—1. **Chlorination.**—The roasted ore, usually in the form of concentrates, is moistened and put into a wooden tub lined with some chlorine-resisting material, such as tar, and provided with a false bottom beneath which a pipe from a chlorine still opens. The tub and the chlorine still are shown in Fig. 33. The attack is continued for some hours in the closed tub, and at the end of the time water is poured in to cover the ore, and the solution of gold chloride filtered. The chlorine should be washed free from

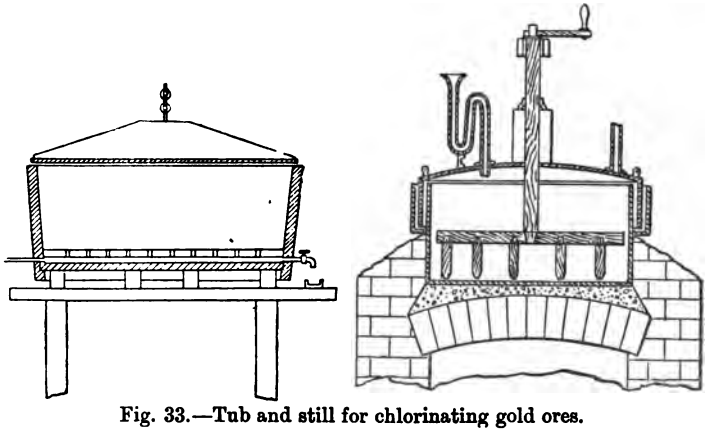


Fig. 33.—Tub and still for chlorinating gold ores.

hydrochloric acid, so that it may attack only the metals present and not the oxides—*e.g.*, ferric oxide from roasted pyrites—nor the sulphides remaining from imperfect roasting, as in the last case H_2S would be evolved and precipitate gold. The necessity for the absence of sulphides makes it requisite that the roasting should be as complete as possible; when alkaline earths —*e.g.*, lime—are present, a chlorinating roasting by the addition of salt is advisable, as otherwise such materials lead to the consumption of chlorine in extracting the gold. The dissolution of the gold is sometimes aided by pressure applied either to the chlorine or hydraulically to the solution in the extracting vessels, and by the use of revolving or tumbling cylinders to agitate the ore during extraction. However obtained, the solution of gold chloride is precipitated by a solution of ferrous sulphate,* by SO_2, or by filtration through charcoal. The cause for the reducing action of the last named is obscure.

2. **Cyanide Extraction.** — Within the last few years it has been found that a weak solution (*e.g.*, 1 per cent. or under) of potassium cyanide can be profitably used for extracting gold, especially from the poor tailings of other processes. The reaction said to occur is—

$$Au + 2KCy + O + H_2O = AuCy.KCy + 2KOH$$

the presence of oxygen or some negative element or radicle being essential. Thus bromine may be used in the form of cyanogen bromide.

The ordinary cyanide process is carried out in the crudest possible way. The tailings are placed in large wooden tubs (holding 500 to 600 tons) and leached with a weak solution of KCy—*e.g.*, 0·25 to 0·5 per cent. After the extraction is complete (this occupying 24 hours or more) the solution is run off and the ore washed, the washing liquors being used for making up fresh solution. The main liquor is run into long wooden boxes filled with zinc turnings which precipitate the gold and allow of the recovery of the metal by roasting and refining in the usual manner. An alternative plan of recovery consists in running the cyanide liquor into a tank filled with iron anodes and sheet lead cathodes upon which the gold is deposited by a feeble current. The cathodes when loaded with gold are removed and cupelled. The anodes are enclosed in bags to retain any Prussian blue formed by the action of the cyanide upon them.

3. **Collection of Gold in a Pyrites Matte.** — The auriferous pyrites is smelted with an alkaline flux (*e.g.*, limestone) to remove quartz; about half the sulphur of the pyrites is volatilised and a matte of ferrous sulphide obtained. This is roasted and smelted with a fresh quantity of pyrites, the siliceous matter of which fluxes the iron oxide formed during the previous roasting.

* $2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3$.

The series of processes is repeated until a matte rich in gold is obtained, when it is again roasted and fused with lead which dissolves out the gold, and is cupelled for the recovery of the precious metal.

Refining of Gold.—However won, the crude gold is run into ingots and is usually refined at the mint where it is coined. The gold obtained by chlorination contains 99·7 to 99·9 per cent. Au, but that from most other processes may be considerably less pure, containing silver as the chief impurity. As both gold and silver are not oxidised in air at any temperature, they are collected together by cupellation and cannot be separated by continuing the process. Advantage can be taken of the ease with which silver unites with sulphur, to remove silver from gold by either of the following processes :—

1. **Removal of Silver by means of Sulphur.**—The silver-gold alloy is granulated, moistened, mixed with 15 per cent. of sulphur, thrown into a red-hot crucible, and fused under a layer of charcoal. Silver sulphide is formed and gold separates. The method is generally used in treating gold-silver-copper alloys, in which case cuprous sulphide is also formed. Separation of the silver takes place on limited oxidation, the sulphur remaining as cuprous sulphide, and an alloy of silver and gold being formed which can be parted by repeating the process, or by some other suitable method.

2. **Removal of Silver by Antimony Sulphide.**—The alloy is fused in a crucible and powdered antimony sulphide thrown in. Two layers are thus formed, the upper a matte of sulphides of antimony, copper, and silver, the lower one of gold alloyed with antimony; this alloy is refined by fusion with borax, nitre, and glass, the antimony being removed as an antimonate.

3. **Removal of Silver as Chloride** (*Miller's Process*).—When chlorine is passed through fused gold the metal is unattacked because the temperature is above the decomposition temperature of gold chloride. Silver chloride on the contrary is stable at this temperature. These principles are applied by passing chlorine through a fireclay pipe to the bottom of the crucible containing the melted gold. A layer of fused silver chloride separates on the surface of the gold, and any antimony, arsenic, lead or bismuth is volatilised as chloride. Formerly a similar effect, as far as removal of Sb, &c., is concerned, was obtained by throwing $HgCl_2$ upon the surface of the melted gold.

4. **Separation by Dissolution of the Silver in Acids** ("**Parting**").—Advantage can be taken of the solubility of silver in nitric acid and the insolubility of gold in the same menstruum for separating the metals, but the process is only efficient when the proportion of silver to gold is not less than 2 : 1, because otherwise the gold left on the surface of the alloy obstructs the action of the acid unduly. In order to ensure this proportion,

the gold generally has to be fused with additional silver. The amount formerly used was sufficient to lower the proportion of gold to one-fourth of the whole, the process of separation being called on that account "quartation." The silver is recovered by precipitation as chloride. The process is now less practised than formerly because of the high price of nitric acid as compared with that of sulphuric acid. Parting by sulphuric acid has consequently nearly displaced the nitric acid method. In this case the proportion of gold should not exceed one-fifth of the silver and more than one-tenth of copper is detrimental. The granulated alloy is boiled with three and a-half times its weight of strong sulphuric acid in a cast-iron retort. When the parting is complete the liquid containing silver sulphate and copper sulphate is decanted, and the gold is washed and fused; the silver is recovered by precipitation with copper. Gold is also parted electrolytically by a process similar to that described for silver (p. 209).

Properties and Uses of Gold.—Gold melts at 1,062° C. = 1,944° F. Its specific gravity is 19·32. It is a most resistant metal, being very inactive chemically, on which account, as well as on account of its comparative rarity, it is suitable for coinage —its chief use. Unlike silver, it is untarnished by sulphur. An arbitrary method for computing the fineness of gold consists in stating the proportion of Au with reference to the standard 24 carats for pure gold. Thus, the sovereign, 22 carats fine, contains 91·66 per cent. of gold and 8·33 per cent. of alloying metal (in England copper, but in Australia silver). The industrial uses of gold are limited by its high price. It withstands the action of sulphuric acid better than does platinum, and is therefore adopted for lining platinum vitriol stills. Being very malleable, it is used for making gold leaf for ornamental gilding. Gold-plating by the electrolysis of the double cyanide of gold and potassium is also largely practised.

PLATINUM AND ITS CONGENERS.

The metals platinum, palladium, rhodium, osmium, ruthenium, and iridium constitute what is known as the platinum group, and occur associated together in the native state in alluvial deposits—chiefly in the Ural district. The composition of native platinum may be gathered from the following analysis :—

	Per cent.
Platinum,	84·30
Rhodium,	3·46
Iridium,	1·46
Palladium,	1·06
Osmium,	1·03
Copper,	0·74
Iron,	5·31
Lime,	0·12
Quartz,	0·60

The ore is often associated with grains of a hard refractory alloy of osmium and iridium (**osmiridium**). The native grains of osmiridium are generally used for the points of pens. Unlike gold, platinum does not readily amalgamate with mercury, so that when gold accompanies the platinum sand it is first extracted by amalgamation.

Platinum has never been found other than native until recently, when a platinum arsenide, $PtAs_2$, **sperrylite**, has been found in the pyritic nickeliferous deposits of the Sudbury mines (see *Nickel*, p. 193).

Winning Platinum from its Ore.—The refractory character and high price of the metals of the platinum group make their winning and separation almost a laboratory operation. The opening up of the ore may be effected by wet or dry methods. By the former process the ore is heated to redness and digested with hydrochloric acid, which dissolves the base metals. It is then treated in retorts with aqua regia, by which palladium, rhodium, platinum, and a little iridium are dissolved; osmic acid passes over into the distillate; and osmiridium, ruthenium, chrome iron ore, and titanic iron ore remain undissolved. The solution containing the platinum is neutralised with sodium carbonate, and the palladium is precipitated from it by mercuric cyanide. The platinum, together with a little iridium, is then precipitated as the double chloride with ammonia, $(NH_4)_2PtCl_6$. When this precipitate is ignited, spongy platinum containing a little iridium is left, and is compressed and melted in a lime furnace heated by the oxyhydrogen jet. The platinum obtained in this manner is hardened by the presence of iridium, an advantage for some purposes.

A more modern process consists in heating platinum ore in a small reverberatory furnace, with galena and some glass. Litharge is then added, and the metallic lead formed by its reaction with the galena (p. 172) dissolves the platinum and its accompanying metals, allowing the osmiridium to sink to the bottom of the charge. The platiniferous lead is run off and cupelled, and the crude spongy platinum fused in an oxyhydrogen furnace, the high temperature of which volatilises any base metals present as impurities, as well as silver, gold, palladium and osmium.

The remaining platinum metals have but few industrial applications, and their extraction need not be described.

Properties and Uses of Platinum.—Platinum is a soft metal of great tenacity; it has a specific gravity of 21·5, and a fusing point of 1,775° C. = 3,227° F. Its chemical inertness makes it of use in the laboratory and chemical works for vessels exposed to strong acids—*e.g.*, vitriol stills. The fact that its coefficient of expansion is nearly identical with that of glass enables platinum wires to be sealed through glass apparatus, as in eudiometers and incandescent electric lamps. Platinum and

platinum-rhodium (an alloy containing 10 per cent. of the latter metal) thermo-electric couples are used in pyrometry (p. 84). The resistance of platinum to corrosion renders it and its iridium alloy (10 per cent. Ir) useful for standard weights and measures.

METALS DIFFICULT OF REDUCTION.

Metals, the oxides of which have high heats of combination, were naturally the last to be reduced in the laboratory, and yet later on an industrial scale. Such metals are manganese, aluminium, magnesium, and the metals of the alkalies and alkaline earths. They are probably all reducible by carbon if the temperature be high enough, but in some cases—*e.g.*, in the case of aluminium—this is so high that an electric furnace is the only means of attaining it, when it becomes difficult to assert that the effect is due to heat alone. The volatility of the metals of the alkalies, and their consequent removal from the sphere of reaction, assists the reducing action of the carbon, and enables them to be used in their turn as reducing agents in methods applied for the reduction of less volatile metals. Owing to the fact that electrical energy can be economically produced of any required voltage to correspond with the heat of combination of the intended electrolyte (p. 87), electrolysis often presents advantages in the reduction of metals of this class. Seeing that many of these metals have a higher heat of combination with oxygen than has hydrogen it follows that the electrolysis of aqueous solutions is generally out of the question, because the water would be the compound chiefly decomposed, and the use of fused salts—*e.g.*, chlorides and fluorides—is, therefore, adopted instead.

The chemical energy represented by a metal of this class in the free state, warrants the *prima facie* conclusion that it would be spontaneously reconverted into oxide on exposure to the atmosphere. This is true of some, notably sodium and potassium, but is not applicable to others—*e.g.*, magnesium and aluminium.

In these instances two causes may be stated for the inertness of the metal. The first and most important is that in a large number of cases of exothermic reactions the starting of the change needs the impress upon the reagents of a small initial charge of energy. This is only a particular case of what is generally true of the conversion of potential into kinetic energy, and chemically may be compared with the detonation of an explosive. Usually this initial change is brought about by raising the temperature of the metal which is capable of vigorous oxidation—*e.g.*, the heating of magnesium wire previous to its deflagration. The second cause, though secondary in kind, may be of importance equal to the first. It is that the metal undergoes superficial oxidation, and when the oxide is unattacked by

atmospheric agencies the coating first formed protects, in great measure, the metal beneath. This is well seen in the case of aluminium.

I. **ALUMINIUM.**—1. **Ores of Aluminium.**—**Corundum**, aluminium oxide, Al_2O_3. This mineral, which is a fairly pure form of crystalline alumina, occurs in India, Siberia, and the United States. It contains about 93 per cent. of Al_2O_3, and is characterised by its extreme hardness (exemplified by that of **emery**, an impure form of the same substance), on which account it is mainly used for abrading purposes. Its comparative rarity and hardness make it unsuitable for use as a source of aluminium.

Bauxite, hydrated oxide of aluminium, $Al_2O_3.H_2O$.—This form of oxide, which is rarely pure, is found in France and Ireland; it varies much in quality, containing

Al_2O_3, ...	30 to 60 per cent.
Fe_2O_3, ...	3 to 25 ,,

the remainder being chiefly silica and water of hydration.

Cryolite, a double fluoride of aluminium and sodium, $Al_2F_6.6NaF$. —This occurs at Ivigtuk in Greenland as a white, crystalline, translucent mineral, which is readily fusible and easily yields aluminium.

The chief ore of aluminium, bauxite, has to be treated for the production of pure alumina before the metal can be won; for this purpose it is fused with sodium carbonate, sodium aluminate being formed and ferric oxide left unattacked. The mass is leached with water and the solution treated with CO_2, whereby alumina and sodium carbonate are produced. Recently, it has been found that a solution of sodium aluminate prepared in this way is sufficiently unstable to have its decomposition determined by the addition of a small quantity of alumina, the caustic soda liberated being incapable of redissolving alumina hydrated to the extent of that thus thrown down. Sodium silicate is not affected under these conditions (as it is by excess of CO_2), and contamination of the alumina with silica is therefore avoided.

2. **Winning of Aluminium.**—Unlike the generality of metals, aluminium cannot be directly reduced by carbon at ordinary furnace temperatures, as the equation $Al_2O_3 + 3C = Al_2 + 3CO$ involves the absorption of 305 Cal. As aluminium alloys with most metals with evolution of heat, the reduction of it in this form—viz., as an alloy—can be attained with a smaller absorption of heat than when the metal itself is reduced, so that when alumina, carbon, and copper are heated to a very high temperature, as in an electric furnace, an aluminium-copper alloy results. An indirect chemical method or a direct application of electrical energy is consequently adopted for the commercial reduction of unalloyed aluminium.

(*a*) **Indirect Reduction by Chemical Means.**—Although no compound of aluminium can be directly reduced by means of

carbon, yet one of its most refractory compounds, the oxide, having the high heat of combination of 392 Cal., can be converted into the chloride (heat of combination 322 Cal.), and this reduced to metal by the action of sodium, itself won by carbon. The process, due to Deville, is now obsolete; it consists in heating a mixture of alumina and carbon in a stream of chlorine, the following reaction occurring:—

$$Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO.$$

The carbon is necessary for supplying, by its union with O, the energy represented by the difference in the formation heats of Al_2O_3 and Al_2Cl_6.

Although aluminium chloride can be obtained by dissolving alumina in hydrochloric acid, it is then an hydrated salt, which is decomposed into alumina and hydrochloric acid when heated. The method given above, or one equivalent thereto, is, therefore, essential for the preparation of anhydrous Al_2Cl_6. By using a mixture of alumina and salt instead of alumina, the double chloride of aluminium and sodium, $Al_2Cl_6.6NaCl$, is obtained, and is a more convenient form for the subsequent reduction to aluminium. The second stage of the reaction consists in heating this double chloride with sodium:—

$$Al_2Cl_6.6NaCl + Na_6 = Al_2 + 12NaCl.$$

A modification of this process consists in the use of cryolite or of aluminium fluoride in place of the double chloride of aluminium and sodium, sodium still being the reducing agent.

(*b*) **Reduction of Aluminium by Electrolysis.**—When aluminium salts are electrolysed in aqueous solution, they do not yield the metal, hydrogen being reduced in preference to aluminium. Fused salts, such as the double chloride of aluminium and sodium, are therefore used. To avoid the cost of a bath of a pure halogen salt of aluminium, needing constant renewal, alumina itself is fed into a bath of fused cryolite, in which case the alumina is dissolved and is decomposed by the current in place of the halogen salt.

The process is carried out in an iron vessel, A (Fig. 34), lined with carbon, serving to contain the electrolyte, B, and to act as the cathode, the current entering by the copper pins, D. Passing through the graphite covers, F, is a bundle of carbon rods, C, immersed in the bath, which is maintained in fusion by the heat generated by the passage of the current; this bundle of rods constitutes the anode and is consumed by the oxygen resulting from the electrolysis of the alumina, fed regularly to the bath during the process. A tap hole, E, at the bottom of the vessel containing the electrolyte serves for the collection of the separated aluminium. The electrical pressure requisite is 5 to 6 volts., the output, of course, depending on the number of ampères sup-

plied at this pressure. The process is conducted where cheap power—*e.g.*, from a waterfall—is obtainable. Noxious gases, due to the fact that the bath contains fluorides, are evolved during the electrolysis. The substitution of aluminium sulphide dissolved in a bath of fused alkaline chloride for aluminium oxide dissolved in a fluoride has been devised, and it presents the advan-

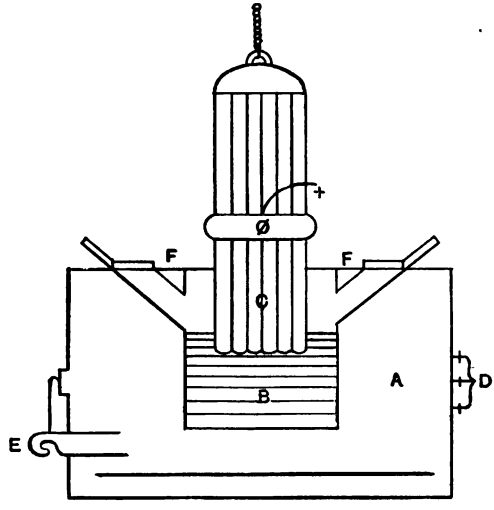


Fig. 34.—Reduction of aluminium by electrolysis: A, Carbon-lined vessel; B, electrolyte; C, carbon rods; D, copper pins; E, tap hole.

tages that the anode is not consumed—as sulphur is liberated there instead of oxygen, and the temperature is too low for the production of CS_2—and that a lower voltage—*e.g.*, 3 volts—is required.

(*c*) **Direct Production of Aluminium Alloys.**—Seeing that aluminium evolves heat in forming alloys, the direct reduction of the metal as a constituent of an alloy is more readily effected than that of aluminium alone. The electric furnace is the chief means of such production; this consists of a horizontal firebrick box lined with charcoal, dipped in lime water to prevent its agglomeration at the high temperature reached. The electrodes project horizontally into the furnace at each end and are heavy carbon rods, which can be fed into the furnace as they are consumed. The charge, consisting of alumina, carbon, and copper, is placed between the electrodes and fused by the heat resulting from the electrical energy supplied, the conversion of which into heat is due to the resistance of the charge. A furnace of industrial size will take about 125 horse-power and an alloy of copper and aluminium, containing 15 to 35 per cent. Al, is obtained. The following is a typical product:—

	Per cent.
Copper,	71·5
Aluminium,	20·1
Silicon,	4·1
Iron,	4·2

In more modern practice the disposition of the furnace is vertical, the carbon lining serving as the lower electrode, the arrangement being somewhat similar to that adopted in the electrolytic process (*v.s.*).

The same process can be adopted for preparing other aluminium alloys—*e.g.*, ferro-aluminium.

3. **Properties and Uses of Aluminium.**—Aluminium is a white metal of specific gravity 2·56, and melting point 654° C. (= 1,209° F.). Although having a high heat of combination with oxygen, it is not readily corroded in air, in the massive state; when finely divided, however, by amalgamation with mercury or alloying with antimony, it oxidises readily. Its inertness when massive is largely due to the protection afforded it by the first film of oxide resulting from its corrosion. When pure (free from silicon and iron) it can be used for cooking vessels and brought freely into contact with food and drink without being attacked to an injurious extent. It is largely used for military fittings on account of its lightness. Pure aluminium has a tensile strength, when cast, of about 5 tons per sq. inch, and when wrought, of 12 to 16 (see p. 30). Its alloys are more useful than the pure metal. Two classes may be distinguished :—(1) Those consisting of 90 per cent. or more Al, the remainder being some foreign metal added to increase the strength of the material without greatly raising its specific gravity. Thus, an alloy containing Al 94 Cu 6, has a specific gravity of 2·82 and a tensile strength of 24·7 tons; one with 2 to 3 per cent. of Ti has a tensile strength of 18 to 26 tons. Similar alloys have been prepared with tin, nickel, zinc, and silver respectively. (2) The other class consists of aluminium bronzes and brasses. They are of the same class as ordinary copper alloys, but improved by the addition of aluminium. Thus, aluminium bronze, Cu 90, Al 10 per cent., may have a tensile strength of 40 tons; aluminium brass, Cu 63, Al 3·3, Zn 33·3 per cent., has a strength, when cast, of 20 tons. Such alloys are not only stronger but less easily corroded than ordinary brasses or bronzes. Aluminium is also used in casting steel, its effect being to reduce the oxides present and to decompose entangled CO; the quantity used is from 4 to 10 ozs. per ton, and may be applied either as the metal itself or as ferro-aluminium containing 10 to 20 per cent. Al. It is also used for adding to zinc in zincing (p. 26) to hinder oxidation of the bath, and in the Parkes process (see *Lead*, p. 179). A great hindrance to the extended application of aluminium has hitherto been the difficulty of solder-

ing it successfully, but this is now partly overcome by the use of solder containing aluminium and the abandonment of fluxes. The refractory character of the oxide, the ease with which the metal is attacked by both acid and alkaline fluxes, and the high specific heat (0·212), no doubt account for this difficulty of soldering.

II. **MAGNESIUM.**—1. **Sources of Magnesium.**—Magnesium is widely distributed in the form of earthy rocks, such as magnesite, $MgCO_3$, dolomite, $MgCO_3.CaCO_3$, and silicates—*e.g.*, **asbestos** and **serpentine.** But none of these is directly available for winning the metal. Large deposits of magnesium salts, such as kieserite, $MgSO_4.H_2O$, carnallite, $MgCl_3.KCl.6H_2O$, and kainite, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$, occur in Strassfurt, which can be worked up to yield a pure magnesium salt suitable for the obtainment of the metal.

2. **Winning of Magnesium.**—Sodium is used as a reducing agent to obtain magnesium from its chloride, in a manner similar to that of the old Deville process for making aluminium (p. 220). The fact that magnesium chloride is more stable than aluminium chloride, enables the former to be obtained anhydrous, mixed with potassium chloride, by heating carnallite. When the double chloride of magnesium and ammonium is substituted for carnallite, $MgCl_2$ itself can be obtained anhydrous, the ammonium chloride being volatilised. Ten parts of the dried carnallite are mixed with one of sodium and one of powdered fluor spar; the mixture is thrown into a red-hot crucible and covered until the main reaction is complete, when magnesium amounting to about three-quarters of the theoretical yield is obtained as a button. The crude metal, which contains silicon, may be purified by distillation, its volatility being similar to that of zinc (B.P. about 1,000° C. = 1,832° F.).

Magnesium can also be won by the electrolysis of fused carnallite, the operation being carried on in an iron crucible, which serves as the cathode, a carbon rod constituting the anode. An indifferent or reducing atmosphere is maintained in the crucible to prevent oxidation of the magnesium, and the anode is surrounded by a fireclay tube through which the chlorine produced by the electrolysis is drawn off.

3. **Properties and Uses of Magnesium.**—Magnesium is a white metal of specific gravity 1·74 and melting point 750° C. = 1,382° F.; it is easily corroded in a moist atmosphere, becoming covered with a white coating of hydrated oxide. It is malleable, and when hot—*e.g.*, at 450° C. = 842° F.—can be drawn into wire and flattened into ribbon. It is largely used in pyrotechny, both as ribbon and powder, and for producing a flash light for signalling and for photographic purposes. Thus its chief value arises from the ease with which it burns in air and the brilliant actinic light which it emits. The product of its combustion in

air contains Mg_3N_2 as well as MgO. It is slowly attacked by water, especially when hot, and readily by dilute acids.

Magnesium has not yet yielded alloys of industrial importance. The pure metal has a tensile strength of about 14·5 tons per square inch, and a compressive strength of about 17 tons. It is employed in the laboratory as a reducing agent, especially in place of zinc, as it is free from arsenic.

III. **MANGANESE.**—1. **Ores of Manganese.**—Manganese is chiefly found as the dioxide MnO_2, both anhydrous, as **pyrolusite**, and hydrated, as **wad. Braunite**, Mn_2O_3 is another of its ores. The sulphide and carbonate are also found.

2. **Winning of Manganese.**—Manganese can be reduced from its oxide by carbon at a high temperature; the metal thus obtained contains carbon. It is more readily prepared, however, by reducing $MnCl_2$ by sodium or magnesium. In the latter case the dried powdered chloride, mixed with twice its weight of KCl, is fused and magnesium introduced in successive portions until an amount of this metal equal to one-sixth of the weight of the manganese chloride has been used.

Recently, manganese has been reduced by aluminium and also by ferro-silicon, a cheaper agent. The process is carried out by heating manganese oxide with ferro-silicon, containing 30 per cent. Si, on a basic hearth or in a basic crucible.*

Manganese is not produced on a large scale save as ferro-manganese, which is obtained by reducing iron ores rich in manganese in a blast furnace. The composition of this alloy is as follows:—

	Per cent.
Mn,	81·24
Fe,	12·00
C,	6·60
Si,	0·09
P,	0·30

It is used in steel making (*q.v.*). Manganese-copper can be produced by heating together copper, oxide of manganese, and carbon, and is used in copper refining to reduce over-oxidised copper in manner analogous with the use of ferro-manganese in steel making (p. 161).

3. **Properties of Manganese.**—It is a greyish-white metal of specific gravity 8·0, readily oxidised by moist air. It fuses at 1,900° C. = 3,452° F. It decomposes water at the boiling point.

IV. **SODIUM.**—Formerly, sodium was obtained by reducing the carbonate with carbon—

$$Na_2CO_3 + C_2 = Na_2 + 3CO.$$

* The ferro-manganese resulting is nearly free from carbon, and can be used for making manganese steel without raising its content of carbon. Ferro-silicon can also be used for reducing NiO, Cr_2O_3, and WO_3.

The reaction is endothermic, according to data determined at the ordinary temperature, 186 Cal. being absorbed; the volatility of sodium no doubt assists the occurrence of the reaction, the product, Na, being spontaneously removed from the sphere of action by distillation. The operation was effected by heating a mixture of 30 parts of sodium carbonate, 13 of charcoal, and 5 of calcium carbonate in a horizontal iron tube connected with an iron condenser opening into a receiver containing mineral oil; a temperature of about 1,500° C. = 2,732° F. was requisite for the distillation. The calcium carbonate was added to pre-

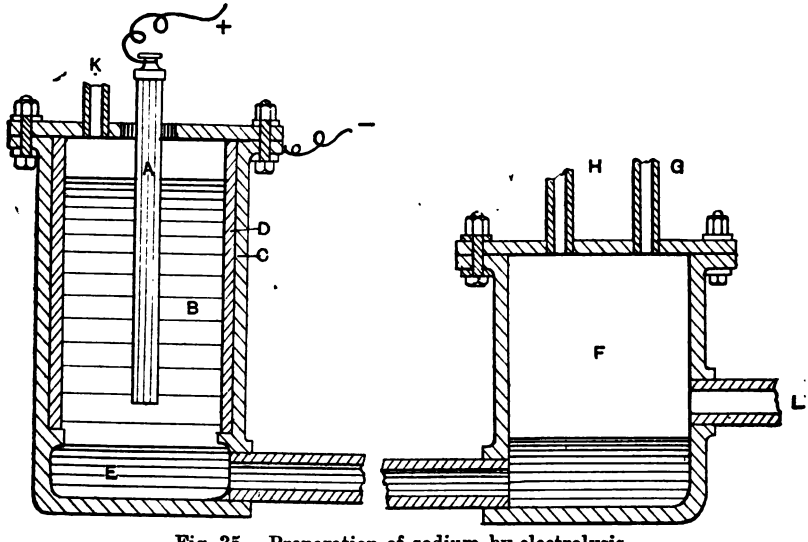


Fig. 35.—Preparation of sodium by electrolysis.

A, Carbon anode; B, bath of fused salt; C, iron vessel lined with magnesia bricks, D; E, fused lead; F, second iron vessel; G, steam supply pipe; H, hydrogen exit pipe.

vent the sodium carbonate from flowing away from the charcoal when fused.

Sodium is now made by Castner's process, which consists in heating caustic soda with one-fifth its weight of "carbide of iron," a substance made by heating iron oxide with tar; the function of the iron in this mixture is to keep the carbon immersed in the fused caustic soda. The reduction of the sodium is said to take place according to the equation—

$$4NaOH + C_2 = Na_2CO_3 + Na_2 + 2H_2 + CO.$$

This reaction is endothermic, requiring the absorption of 106 Cal., considerably less than in the case of the old process. The operation is carried out in steel crucibles set in a furnace heated by

producer gas, a temperature of about 800° C. = 1,472° F. being requisite. The crucibles are covered with domes carrying an exit pipe, through which the sodium distils into a receiver containing mineral oil. A yield of about 90 per cent. is claimed. The sodium carbonate obtained as a bye-product is leached out of the spent contents of the crucible, causticised, and used again.

A recent process for preparing sodium by the electrolysis of fused sodium chloride is that devised by Vautin, and consists in passing a current from a carbon anode, A (Fig. 35), into a bath of salt (kept fused by the heat generated by the current), B, contained in an iron vessel, C, the upper part of which is lined with magnesia bricks, D. The cathode is a pool of fused lead, E, at the bottom of the iron vessel, the current being conveyed to the lead through the iron vessel, as shown in the figure. Sodium is liberated at the cathode, and dissolves in the lead, from which it can be recovered as caustic soda by passage into a second iron vessel, F, connected with the first, as shown, it being there brought into contact with steam supplied through the pipe G, the hydrogen thus generated escaping through the second pipe, H. The fused caustic soda is withdrawn through the pipe L. The chlorine liberated at the anode, A, escapes through the pipe K, and may be used for the manufacture of bleaching powder. By distilling the lead-sodium alloy instead of treating it with steam, sodium may be obtained. A lower voltage (about 2 volts) than when an aqueous solution of NaCl is electrolysed, for the production of alkali and bleach (*q.v.* Vol. II.), is required.

Sodium is a white metal with a pink tinge, of specific gravity 0·97; melting point, 95° C. = 203° F.; and boiling point, 742° C. = 1,368° F. It oxidises on exposure to air, and decomposes water; it is kept under mineral oil, generally a light petroleum. It is used chiefly for reducing other metals—*e.g.*, magnesium—for making sodium amalgam (see *Gold extraction*, p. 213), and for making **sodium peroxide**. This is effected by placing the sodium on aluminium trays which are made to traverse a flue through which a current of dried and purified air is travelling in the opposite direction. The metal is thus systematically oxidised to Na_2O_2. Na_2O_2 is used as a general oxidant, particularly for bleaching, in those cases in which H_2O_2 was formerly employed.

Potassium may be made by methods similar to those employed for producing sodium. As in the case of sodium, the reduction of the carbonate by carbon is endothermic, an absorption of 194 Cal. taking place. The preparation of the metal is somewhat dangerous, from the formation of a black explosive compound of potassium and carbon monoxide, $K_6(CO)_6$. Potassium is a white metal of a specific gravity 0·87; melting point 62° C. = 144° F.; and boiling point 667° C. = 1,233° F. It forms an alloy with sodium which is liquid at the ordinary temperature, and has lately been used for the construction of high-range thermometers, indicating temperatures up to 600° C. = 1,112° F.

INDEX.

A

Accumulator, 91.
Acid bricks, 8.
,, Fatty, in oils, 116.
Aciertype, 149.
Aerial cement, 10.
Aggregate, 9.
Alabaster, 5.
Alloy, Iron-nickel, 24.
Alloys of aluminium, 24, 222.
,, of copper, 20, 169.
,, of lead, 180.
,, of nickel, 197.
,, of zinc, 184.
Aludels, 200.
Alumina, 219.
,, Chemical reduction of, 219.
,, Electrolytic reduction of, 220.
Aluminium, 90.
,, alloys, 24, 222.
,, brass, 23, 222.
,, bronze, 23, 222.
,, chloride, 220.
,, Corrosion of, 42.
,, Melting point of, 222.
,, Ores of, 218.
,, oxide, 219.
,, sodium chloride, 220.
,, soldering, 222.
,, Specific gravity of, 222.
,, ,, heat of, 223.
,, Uses of, 222.
Amalgamated zinc, 89.
Amalgamation of gold, 212.
Amorphous antimony, 190.
Analysis of aluminium bronze, 222.
,, of basic pig, 145.
,, ,, steel, 146.
,, of Bessemer steel, 143.
,, of boiler incrustations, 100, 102, 103, 107.
,, of calcareous water, 101.
,, of cast iron, 14.
Analysis of cast nickel, 197.
,, of clay ironstone, 129.
,, of coal, 50, 52.
,, of copper fire-box, 20.
,, of fireclay, 7.
,, of ferro-manganese, 224.
,, of hæmatite, 127.
,, of magnesite, 9.
,, of magnetite, 128.
,, of meteoric iron, 126.
,, of millstone grit, 3.
,, of mine water, 103.
,, of native platinum, 216.
,, of nickel ore, 194.
,, of peaty water, 101.
,, of rust, 40.
,, of sea-water, 102.
,, of serpentine, 5.
,, of spathic iron ore, 128.
,, of water gas, 71.
,, of wood creosote, 47.
,, of wrought iron, 16.
Angus Smith's composition, 44.
Anthracite, 50.
Anti-fouling compositions, 45.
Anti-incrustators, 112.
Antimony, Amorphous, 190.
,, Crude, 189.
,, Electrolytic winning of, 190.
,, flux, 190.
,, fume, 190.
,, in galena, 170.
,, Melting point of, 190.
,, Native, 188.
,, ochre, 188.
,, Red, 188.
,, Reduction of, by iron, 189.
,, Refining, 190.
,, Regulus of, 189.
,, Self reduction of, 189.
,, Sources of, 188.
,, Star, 190.
,, sulphide, 188.

Antimony, sulphide, Liquation of, 188.
,, ,, process for gold refining, 215.
,, ,, smelting in blast furnace, 190.
,, ,, Specific gravity of, 190.
,, Uses of, 190.
,, Winning of, 188.
Argentite, 202.
Armatures, Iron for, 93.
Arsenical nickel ores, Treatment of, 196.
Arsenide of platinum, 217.
Artificial stone, Efflorescence on, 33.
Astatki, 57.
,, Calorific value of, 58.
Atomic volumes of impurities in iron, 153.
Augustin's process for silver, 207.
Autogenous soldering, 34.
Axle grease, 120.
,, Water in, 120.
Azurite, 154.

B

Babbitt's metal, 24.
Ballast, 10.
,, Burnt, 10.
Barilla copper, 154.
Barrel process for silver, 206.
Basic lining, 145, 146.
,, pig, Analysis of, 146.
,, refining of copper, 161.
,, steel, Analysis of, 146.
,, zinc carbonate, 181.
Bath stone, 5.
Battery, Grove's gas, 92.
Bauxite, 219.
Bearings, Oils for, 116.
"Bears" in blast furnaces, 135.
Belgian zinc retorts, 182.
Bell metal, 170.
Bessemer blow, Stages of, 144.
,, converter, 142.
,, pig, 143.
,, steel, Analysis of, 143.
Bessemerising copper, 163.
,, galena, 175.
,, nickel matte, 194.
"Bicarbonates" in water, 99.
Bichromate cell, 88.
Biotite, 4.
Bismuth, Desilverising, 192.
,, glance, 191.
,, Impurities in, 192.
Bismuth, Liquation of, 191.
,, Melting point of, 191.
,, Native, 191.
,, ochre, 191.
,, Refining, 192.
,, Sources of, 191.
,, Specific gravity of, 192.
,, Uses of, 192.
,, Winning of, 191.
Bismuthite, 191.
Black band ore, 128.
,, charcoal, 56.
,, copper, 160.
,, earthy cobalt, 198.
,, -jack, 181.
,, litharge, 192.
,, tin, 186.
Blast furnace, 130.
,, ,, balance sheet, 134.
,, ,, Bears in, 135.
,, ,, Boshes of, 130.
,, ,, Burden of, 132.
,, ,, coke, 134.
,, ,, Crucible of, 130.
,, ,, Cyanides from, 135.
,, ,, Efficiency of, 135.
,, ,, for antimony, 190.
,, ,, Gases of, 131.
,, ,, Reactions in, 134.
,, ,, slag, 133.
,, ,, stack, 130.
,, ,, throat, 130.
,, ,, Titanium compound in, 135.
,, ,, twyers, 131.
Blende, 181.
,, nickel, 193.
Blister copper, 159, 160.
,, steel, 147.
Bloom cobalt, 197.
Blown oils in lubricants, 119.
Blue malachite, 154.
,, metal, 159.
,, water, 165.
Bog iron ore, 127.
Boiler compositions, 112.
,, incrustations, 100.
,, plates, Corrosion of, 107.
,, ,, Protection of, 108.
Boiling point of cadmium, 185.
,, ,, magnesium, 223.
,, ,, mercury, 202.
,, ,, potassium, 226.
,, ,, sodium, 226.
,, ,, sulphur, 82.
,, ,, zinc, 82.
Boric anhydride, Melting point of, 82.
Boshes of blast furnace, 130.

Bottoms, Copper, 162.
Boucherie's process, 46.
Bower-Barff process, 44.
Boxes, Pointed, 212.
Brard's test, 32.
Brass, 21, 23, 169.
,, Aluminium, 222.
,, Strength of, 22.
Braunite, 224.
Brazing, 36.
,, Electrical, 36.
Brick, Efflorescence on, 33.
Bricks, 6.
,, Acid, 8.
,, Basic, 8.
,, Bauxite, 8.
,, Blue, 7.
,, Carbon, 8.
,, Chromite, 8.
,, Dinas, 7.
,, Gault, 7.
,, Ganister, 7.
,, Magnesia, 8.
,, Neutral, 8.
,, Red, 6.
,, Refractory, 9.
,, Stock, 6.
,, Stourbridge, 7.
Brin's oxygen process, 75.
Briquettes, 56.
Britannia metal, 188.
Brittle silver ore, 202.
Bromide of silver, 203.
Bronze, aluminium, Analysis of, 222.
,, coinage, Composition of, 170.
,, Patina of, 41.
Bronzes, 170.
Brown charcoal, 56.
,, coal, 50, 54.
,, ,, Calorific value of, 55.
,, ,, Composition of, 55.
,, hæmatite, 127.
Browse, 174.
Buddle, 212.
Bull metal, 23, 170.
Bunsen cell, 88.
Burden of blast furnace, 132.
Burnett's fluid, 46.

C

Cadmium, 185.
,, Boiling point of, 185.
,, Melting point of, 185.
,, silver electroplating, 209.
,, Specific gravity of, 185.
Calamine, 181.
,, Electric, 181.
Calcareous stones, 1, 4.
Calcareous waters, 99.
,, ,, Analyses of, 101.
Calcination of copper ore, 156.
,, of ores, 124.
Calcium carbide, 78.
,, carbonate, Solubility of, 108.
,, sulphate in water, 99.
Californian mercury process, 200.
Calorific value of coals, 49.
Calorimeter, 51.
Calorimetric pyrometer, 85.
Cannel, 50.
Carbide carbon, 149.
,, of calcium, 78.
,, of iron, 151.
,, ,, (Castner's), 225.
,, of silicon, 78.
Carbon, 89.
,, bricks, 8.
,, Forms of, in iron, 149,
,, "hardening," 149.
,, Melting point of, 82.
,, monoxide potassium compound, 226.
,, Oxidation of, 64.
,, percentage in steel, 153.
Carbonate of lead, 171.
,, of zinc, 181.
Carbonic acid, "Free," 99.
,, ,, "Half-bound," 99.
Carboniferous limestone, 5.
Carrara marble, 4.
Case-hardening of iron, 148.
Cassiterite, 185.
Cast crucible steel, 148.
,, iron, Grey, 14, 135.
,, ,, Malleable, 14, 148.
,, ,, Mottled, 14, 135.
,, ,, White, 135.
,, nickel, Analyses of, 197.
,, zinc, 184.
Castings, Steel, 19.
Castner's "carbide of iron," 225.
,, sodium process, 225.
Castor oil, Viscosity of, 115.
Cause of hardness in steel, 152.
Cell, Faure, 91.
,, Planté, 91.
Cells, Galvanic, 87.
,, Primary, 90.
,, Secondary, 90.
,, Storage, 90.
Cement, Aerial, 10.
,, briquettes, 12.
,, copper, 165.
,, Fineness of, 11.
,, Hydraulic, 10.
,, mortar, 9.
,, Portland, 10.

Cement, Puzzuolana, 10.
,, Roman, 10.
,, Setting time of, 12.
,, silver, 208.
,, Slag, 10.
,, Soundness of, 13.
,, Specific gravity of, 11.
,, steel production, 147.
,, Tensile strength of, 13.
,, testing, 11.
,, ,, machine, 12.
Cementation process, 147.
Cerussite, 171.
Charcoal, Black, 56.
,, Brown, 56.
Charred wood, 47.
Checked combustion, 61.
Chemical attack of structural materials, 38.
,, reduction of aluminium, 219.
,, ,, of magnesium, 223.
Chilled iron, 137.
Chloride of aluminium, 220.
,, ,, and sodium, 220.
,, of silver, 202.
,, of tin, 188.
Chlorination, 213.
Chlorine gas battery, 93.
,, process for gold refining, 215.
Chromite bricks, 8.
Chromium steel, 19.
Cinnabar, 198.
,, Specific gravity of, 198.
,, treatment for mercury, 201.
Clark's process, 110.
Classification of irons, 138.
,, of ores, 123.
Claudet process for silver, 208.
Clay ironstone, 128.
,, ,, Analysis of, 129.
Close regulus, 161.
,, test for oils, 118.
Coal, Classification of, 49.
,, creosote, 46.
,, gas as a fuel, 60.
,, ,, Calorific value of, 62.
,, ,, Explosion of, 62.
,, ,, products of combustion, 61.
,, Impurities of, 52.
,, Nitrogen in, 52.
,, washing, 53.
,, weathering, 53.
Coals, Analyses of, 50.
,, Brown, 54.
,, Earthy brown, 55.
,, Specific gravity of, 50.
,, Yield of coke from, 49.
Coarse copper, 159.
,, metal, Calcination of, 158.
,, ,, Fusion for, 157.
,, solder, 37.
Cobalt, 197.
,, Black earthy, 198.
,, bloom, 197.
,, glance, 197.
,, Melting point of, 198.
,, pyrites, 198.
,, Separation of, from nickel, 196.
,, Specific gravity of, 198.
,, speiss, 197.
,, Tin white, 197.
,, Uses of, 198.
Coinage, Bronze, 170.
Coke, 53.
,, Ash of, 53.
,, Specific gravity of, 54.
,, Uses of, 54.
,, for blast furnace, 134.
Cold blow, 71.
Colouring metals, 41.
Composition, Angus Smith's 44.
Compositions, Anti-fouling, 45.
Compo. tube, 181.
Compressive strength of magnesium, 224.
Concentrates, Gold, 213.
Concentration of gold ore, 210.
,, of iron ore, 130.
Concrete, 9.
,, Efflorescence on, 33.
,, Destruction of, 38.
Condensation of mercury, 200.
Conductivity of copper, 169.
Converter, Basic lining for, 145.
,, Bessemer, 142.
Copper, 20.
,, alloys, 20, 169.
,, Barilla, 154.
,, Bessemerising, 163.
,, Best selected, 161.
,, bismuth glance, 191.
,, Black, 160.
,, Blister, 159.
,, bottoms, 162.
,, Cement, 165.
,, Coarse, 159.
,, Diagram of Welsh, process, 161.
,, Dry, 160.
,, Dry process for, 154.
,, Electrical conductivity of, 169.
,, Electrolytic processes for, 166, 167.
,, Extraction of, from pyrites, 165, 166.

Copper fire-box analysis, 20.
,, Influences of impurities on, 20, 168.
,, German smelting process, 162.
,, glance, 154.
,, Kernel roasting for, 156.
,, Manhés process, 164.
,, Mansfeld process, 162.
,, matte for silver extraction, 205.
,, Melting point of, 82.
,, Moss, 159.
,, Native, 154.
,, ores, 154.
,, ,, Calcination of, 156.
,, Oxygen in, 20.
,, poling, 160.
,, pyrites, 154.
,, roasting furnace, 156.
,, refinery slag, 160.
,, sand, 154.
,, Scorification of, 160.
,, smoke, 156.
,, steam pipes, 21.
,, Tinned, 41.
,, Toughening, 161.
,, touch-pitch, 160.
,, Uses of, 168.
,, Welsh process for, 155, 162.
,, Wet extraction of, 165.
Corrosion of aluminium, 42.
,, of copper, 40.
,, of lead, 42.
,, of metals, 39.
,, of nickel, 42.
,, of zinc, 41.
Corundum, 219.
Cosmical energy, 96.
Cradle for gold washing, 210.
Creosote, Wood, 46.
Creosoting, 46.
Critical temperature of iron, 151.
Crucible cast steel, 148.
,, of blast furnace, 130.
,, steel, Analysis of, 148.
Crude antimony, 189.
,, iron, Purification of, 138.
,, lead, Analysis of, 176.
Cryolite, 219.
Crystalline structure of steel, 153.
Cupellation hearth, 205.
,, of lead for silver, 204.
Cupola, 15.
Cupriferous pyrites, 166.
,, schists, 154.
Cuprite, 154.
Current density for copper deposition, 167.
Cyanide extraction of gold, 214.
,, from blast furnace, 135.
Cylinder oil, Viscosity of, 117.

D

Daniell's cell, 87.
Delta metal, 23, 170.
Depolarisation, 87.
Depolariser, Solid, 88.
Desilverising bismuth, 192.
,, lead, 176, 178.
Destruction of concrete, 38.
Desulphurising pig iron, 144.
Dinas bricks, 7.
Dissolved oxygen, Corrosive action of, 105.
Distillation of magnesium, 223.
,, of metals, 126.
,, of sodium, 225.
,, of zinc from ore, 183.
Dolomite, 6.
Double-shear steel, 148.
"Doubling," 189.
Dowson gas, 71.
Dressing ores, 124.
,, tin ores, 185.
"Dry" copper, 160.
Dry extraction, General methods of, 124.
,, process for copper, 154.
,, puddling, 140.
Ductility, Test for, 17.
Dynamo, Economy of, 93.

E

Earthy brown coal, 35.
Economy, Energetic, 96.
,, Monetary, 96.
Efficiency, 92.
,, of blast furnace, 135.
,, of gas engine, 62.
Efflorescence on artificial stone, 33.
,, ,, brick, 33.
,, ,, concrete, 33.
Elastic limit, 17.
Electrical brazing, 36.
,, conductivity of copper, 169.
,, production of aluminium alloys, 221.
,, transmission of energy, 94, 97.
,, welding, 35.
Electric calamine, 181.
,, furnace, 77.
,, resistance pyrometer, 83.

Electrolytic copper processes, 166, 167.
,, iron, 148.
,, parting, 216.
,, purification of iron, 147.
,, reduction of aluminium, 220.
,, ,, of magnesium, 223.
,, refining of copper, 166, 167.
,, ,, of lead, 180.
,, winning of antimony, 190.
,, ,, of zinc, 184.
Electroplating, 209.
Emery, 219.
Enamelled iron, 43.
Energy, Cosmical, 96.
,, Electrical, 86.
,, Kinetic, 93.
,, Sources of, 48.
,, Sun's, 96.
,, Transmission of, 96, 97.
,, Wind, 95.
Extraction, Dry, general methods, 124.
,, of bismuth, Wet, 192.
,, of copper, Wet, 165.
,, of iron, Principles of, 129.
,, of silver by copper matte, 205.
,, ,, by lead, 204.
,, ,, by mercury, 206.

F

Fahlerz, 198.
Fahnehjelm light, 73.
"Fatigue" of metals, 34.
Fatty acids in oils, 116.
Fatty lubricating oils, 114.
Faure cell, 91.
Felspar, 3.
Ferro-chromium, 137.
Ferro-manganese, 137.
,, Analysis of, 224.
Ferro-silicon, 136.
Ferrous carbonate, 128.
Ferruginous water, Softening of, 110.
Fettling, 140.
Fine metal, Fusion for, 158.
Fine solder, 37.
Fireclay, Analyses of, 7.
Firing point of oils, 118.
Flagstone, Yorkshire, 2.
Flashing point of oils, 117, 118.
Flintshire process for lead, 172.
Flux, Antimony, 190.
Fluxes for soldering, 37.
Foil, Tin, 188.
Forms of carbon in iron, 149.
"Free" carbonic acid, 99.
Freestone, 2.
Freiberg process for lead, 176.
Frue vanner, 213.
Fuel, Definition of, 48.
,, Gaseous, 60.
,, Liquid, 57.
,, "Patent," 56.
,, Waste of, 104.
,, Wood as, 56.
Fume, Antimony, 190.
,, Lead, 174.
,, Zinc, 182.
Furnace, Blast, 130.
,, for lead, 173.
,, Reverberatory, for copper, 156.
Fusible metal, 193.

G

Galena, 170.
,, Antimony in, 170.
,, Bessemerising, 175.
,, Gold in, 170.
,, Silver in, 170.
,, smelting methods, 172.
,, Specific gravity of, 171.
Galvanic action causing rust, 40.
,, cells, 87.
,, corrosion, 107.
,, protection, 45.
Galvanised iron, 26.
Gangue, defined, 124.
Ganister, 7.
Garnierite, 193.
Gas batteries, 92, 93.
,, Dowson, 71.
,, engine, 62.
,, Natural, 73.
,, Producer, 65.
,, Water, 71.
Gaseous fuels, 60.
Gases, Blast furnace, 132.
Gasolene for engines, 59.
Gault bricks, 7.
General methods of dry extraction, 124.
Generator gas, 63.
German copper smelting process, 162.
German silver, 197.
Gerstenhöfer kilns, 156.
Gilchrist-Thomas process, 145.

Glance, Bismuth, 191.
,, ,, copper, 191.
,, Cobalt, 197.
,, Copper, 154.
,, Nickel, 193.
Glass-lined pipes, 44.
Gneiss, 4.
Gold, 209.
,, amalgamation, 212.
,, chlorination, 213.
,, collection in pyrites matte, 214.
,, concentrates, 213.
,, "cradle," 210.
,, Electrolytic parting of, 216.
,, extraction by cyanide, 214.
,, in galena, 170.
,, Melting point of, 82.
,, Native, 209.
,, ore concentration, 210.
,, Parting, 215.
,, plating, 216.
,, purification, 214.
,, refining, 215.
,, slimes, 212.
,, Sources of, 209.
,, Specific gravity of, 216.
,, stamps, 211.
,, standard, Composition of, 216.
,, Uses of, 216.
Grain tin, 187.
Granite, 3.
,, Syenitic, 3.
Granitza mercury furnace, 201.
Grease, Axle, 120.
,, Rosin, 120.
Greenstone, 4.
Grey copper ore, 154.
,, iron, 135.
,, ,, Analysis of, 136.
,, ,, Specific gravity of, 136.
Grouting, 9.
Grove cell, 88.
Grove's gas battery, 92.
Gun metal, 22, 170.

H

HÆMATITE, Brown, 127.
,, Red, 127.
Hæmatites, Analyses of, 127.
"Half-bound" carbonic acid, 99.
"Hardening" carbon, 149.
Hardening steel, 150, 153.
"Hardhead," 187.
Hardness of steel, 152.
,, of water, 100.
,, Measurement of, 30.
,, Permanent, 100.
,, Temporary, 100.
Hard soldering, 36.
"Hard" water, 100.
Harvey's process, 148.
"High" system of lead desilverising, 177.
Hoepfner's copper process, 167.
Hornblende, 3.
Horn silver, 202.
Hot blast stove, 131.
,, Temperature of, 132.
Hot blow, 71.
Hydraulic cement, 10.
,, lime, 10.
,, mining, 211.
Hydrogen, 92, 93.
,, in electrolytic iron, 148.
,, manufacture, 74.

I

IDRIAN mercury furnace, 199.
Improving lead, 176, 178.
Impurities in bismuth, 192.
,, in blister copper, 160.
,, in brass, 169.
,, in crude tin, 187.
,, in crude zinc, 184.
,, influence on copper, 168.
,, ,, on iron, 148.
,, in iron, Atomic volumes of, 153.
Incrustation from sea water, 102, 103.
,, Oily, 106, 107.
Industrial temperatures, 83, 85.
Ingot iron, 18.
,, ,, Analysis of, 147.
,, ,, Tensile strength of, 19.
Influence of temperature on viscosity, 115.
Injury to boilers, 104.
Iodide of silver, 203.
Iridium, Melting point of, 82.
,, platinum, 218.
Iron, 13, 90, 149.
,, Atomic volume of impurities in, 153.
,, Behaviour of, on cooling, 149.
"Iron black," 190.
Iron carbide, 151, 225.
,, Case-hardening of, 148.
,, cast, Analyses of, 14.
,, ,, Malleable, 148.
,, Chilled, 137.
,, Critical temperature of, 151.
,, crude, Purification of, 138.
,, Electrolytic, 148.
,, ,, purification of, 147.
,, Enamelled, 43.
,, extraction, Principles of, 129.

Iron for armatures, 93.
,, Forms of carbon in, 149.
,, Foundry pig, 14.
,, Fusing point of, 149.
,, Galvanised, 26.
,, Grey cast, 14, 135.
,, ,, ,, Analysis of, 136.
,, ,, ,, Specific gravity of, 136.
,, Influence of impurities on, 148.
,, Ingot, 15, 147.
,, Lead coating for, 27.
,, Malleable cast, 14.
,, meteoric, Analysis of, 126.
,, Mottled cast, 14, 135.
,, Native, 126.
,, nickel alloy, 24.
,, ore, Concentration of, 130.
,, ,, Preparation of, for smelting, 129.
,, ,, roasting, 130.
,, ores, 126.
,, Paints for, 44.
,, Pig, 135.
,, ,, desulphurising, 144.
,, puddled, Structure of, 142.
,, Preservation of, 43.
,, pyrites, 129.
,, ,, nickeliferous, 193.
,, reduction, 130.
,, Rusting of, 39.
,, Specific gravity of, 149.
,, Tinned, 27.
,, White, 135, 136.
,, "whitening," 139.
,, Wrought, 15.
,, ,, Analysis of, 141.
,, zinc alloys, 184.
,, zinced, 26.
Irons, Classification of, 138.

K

Kassner's oxygen process, 76.
Kelp-salt, 189.
Kentish rag, 5.
Kermes mineral, 188.
"Kernel-roasting" for copper, 156,
Kerosene for engines, 59.
"Killed" spirits of salt, 37.
Kiln, Gerstenhöfer, 156.
,, Step grate, 55.
Kinetic energy, Natural form of, 93.
"Kish," 135.
Kiss process for silver, 208.
Kupfer-nickel, 193.
Kyanising, 46.

L

Lard oil, Viscosity of, 115.
Lead alloys, 180.
,, Analysis of Freiberg crude, 176.
,, as a solvent, Extraction of silver by, 204.
,, burning, 34.
,, carbonate, 171.
,, Chief sources of, 171.
,, coating for iron, 27.
,, Commercial analysis of, 180.
,, Corrosion of, 42.
,, Cupellation of, for silver, 204.
,, Desilverising, 176.
,, ,, Parkes' process of, 178.
,, ,, Pattinson's process of, 177.
,, Electrolytic refining of, 180.
,, Flintshire process for, 172.
,, Freiberg process for, 176.
,, fume, 174.
,, Improving, 176.
,, ,, by Pattinson process, 178.
,, Liquation of, 176.
,, Melting point of, 82, 180.
,, ores for smelting, Preparation of, 171.
,, Ores of, 170.
,, Per cent. of, in crude zinc, 184.
,, Precipitation process for, 175.
,, Reduction of, by carbon, 175.
,, ,, ,, by iron, 175.
,, Scotch hearth for, 174.
,, slag, 175.
,, Softening, 176.
,, Solubility of, in zinc, 178.
,, ,, ,, zinc in, 178.
,, Specific gravity, 180.
,, sulphide, 170.
Leclanché cell, 88.
Levigation, 124.
Lichens on stone, 33.
Light, Fahnehjelm, 73.
,, red silver ore, 202.
,, Welsbach, 73.
Ligneous brown coal, 55.
Lignite, 50.
Lime, Hydraulic, 10.
,, Treatment of cinnibar by, 201.
Limestone, 5.
,, Carboniferous, 5.
,, Lias, 5.
,, Oolitic, 5.
Limonite, 127.
Lining, Basic, 146.
,, ,, of converter, 145.

Liquation of antimony sulphide, 188.
,, of bismuth, 191.
,, of lead, 176.
Liquid fuel, 57.
Litharge, Black, 192.
Local corrosion of boiler plates, 107.
Looking glasses, "Silvering," 202.
Low system for desilverising lead, 177.
Low temperature heat, Utilisation of, 66.
Lubricants, 114.
,, Blown oils in, 119.
,, Corrosion induced by, 120.
,, Solid, 119.
Lubricating oils, Flashing point of, 117.
,, ,, Mineral, 117.
,, ,, Mixed, 118.

M

Machinery oil, Viscosity of, 117.
Magistral, 207.
Magnesite, Analysis of, 9.
Magnesium, Boiling point of, 223.
,, carbonate, Solubility of, 108.
,, Chemical reduction of, 223.
,, chloride in water, 102.
,, Compressive strength of, 224.
,, Distillation of, 223.
,, Electrolytical reduction of, 223.
,, limestone, 6.
,, Melting point of, 223.
,, Sources of, 223.
,, Specific gravity of, 223.
,, Tensile strength of, 224.
,, Uses of, 223.
,, Winning of, 223.
,, Working temperature for, 223.
Magnetic separators, 130.
Magnetite, 127.
,, Analyses of, 128.
Malachite, 154.
,, Blue, 154.
Malleable cast iron, 148.
Malms, 6.
Manganese bronze, Composition of, 170.
,, Melting point of, 224.
,, Ores of, 224.
,, steel, 20, 152.
Manganese, Winning of, 224.
Manhés copper process, 164.
Mansfeld copper process, 162.
,, process for silver, 162.
Marble, 4.
,, Carrara, 4.
"Market pot," 177.
Massenez process, 144.
Materials, Roofing, 25.
,, Strength of, 29.
Matthey's refining process for bismuth, 192.
Measurement of temperature, 78.
Mechanical puddling, 141.
Mechanism of oxidation of carbon, 64.
Melting point of aluminium, 222.
,, of antimony, 190.
,, of bismuth, 191.
,, of boric anhydride, 82.
,, of cadmium, 185.
,, of carbon, 82.
,, of cobalt, 198.
,, of copper, 82.
,, of gold, 82, 216.
,, of iridium, 82.
,, of lead, 82, 180.
,, of magnesium, 223.
,, of manganese, 224.
,, of nickel, 197.
,, of palladium, 82.
,, of platinum, 82, 217.
,, of potassium, 226.
,, ,, bromide, 82.
,, ,, chloride, 82.
,, ,, iodide, 82.
,, ,, sulphate, 82.
,, of silver, 82, 209.
,, of sodium, 226.
,, ,, chloride, 82.
,, ,, sulphate, 82.
,, of solder, 181.
,, of tin, 187.
,, of zinc, 82, 184.
Melting points, Scale of, 82.
Merchant bar, 15.
Mercuric sulphide, 198.
Mercury as a solvent, Extraction of silver by, 206.
,, Boiling point of, 82, 202.
,, Californian process, 200.
,, Condensation of, 200.
,, furnace, Idrian, 199.
,, Native, 198.
,, Purification of, 201.
,, Quickening, 213.
,, Solidifying point of, 202.
,, Sources of, 198.
,, Specific gravity of, 202.
,, Uses of, 201.

Mercury, Winning of, 198.
Meta-cinnabar, 198.
Metal, Babbitt's, 24.
,, Blue, 159.
,, Bull, 23.
,, colouring, 49.
,, Delta, 23.
,, Fusible, 193.
,, Gun, 22.
,, "Pimple," 159.
,, Red, 21.
,, slag, 159.
,, Structural, 13.
,, "White," 159.
,, woods, 193.
,, Yellow, 22.
Metals, Corrosion of, 39.
,, difficult of reduction, 218.
,, ,, ,, Oxidation of, 218.
,, Distillation of, 126.
,, "Fatigue" of, 34.
,, White, 159.
Meteoric iron, Analysis of, 126.
Mexican process for silver, 206.
Mica, 3.
Mild steel, 18.
Miller's chlorine process for refining gold, 215.
Millstone grit, Analysis of, 2, 3.
Mineral lubricating oils, 117.
Mine water, Analysis of, 103.
,, Corrosive effect of, 103.
Mixed lubricating oils, 118.
,, ores, 123.
Mond's gas battery, 92.
Monier system, 10.
Mortar, 11.
,, Cement, 9.
Mottled iron, 135.
"Moss" copper, 159.
Muntz metal, 22.

N

Native antimony, 188.
,, bismuth, 191.
,, copper, 154.
,, gold, 209.
,, iron, 126.
,, platinum, Analysis of, 216.
,, mercury, 198.
,, silver, 202.
Natural gas, 73.
,, ,, Analysis of, 73.
Neatsfoot oil, Viscosity of, 115.
Neutral bricks, 8.
New Caledonian nickel ore, Treatment of, 195.
Nickel, 24.
,, alloys, 197.
,, Antimonial, 193.
,, blende, 193.
,, carbonyl, 193.
,, cast, Analyses of, 197.
,, Corrosion of, 42.
,, glance, 193.
,, matte, Bessemerising of, 194.
,, Melting point of, 197.
,, ores, arsenical, Treatment of, 196.
,, ,, European, Treatment of, 195.
,, ,, Sudbury, Analyses of, 194.
,, ,, ,, Treatment of, 194.
,, oxide, Reduction of, 196.
,, plating, 45.
,, Sources of, 193.
,, Specific gravity of, 197.
,, speiss, 196.
,, ,, Separation of cobalt from, 196.
,, steel, 19, 152.
,, ,, Effect of cooling on, 152.
,, Uses of, 197.
,, Winning of, 193.
Nickeliferous iron pyrites, 193.
Nickel, Kupfer-, 193.
Nitrogen in coal, 52.

O

Ochre, Antimony, 188.
,, Bismuth, 191.
Oil engines, 59.
,, machinery, Viscosity of, 117.
"Oil pulp," 119.
Oil, spindle, Viscosity of, 117.
"Oil thickeners," 119.
"Oils, Blown," in lubricants, 119.
,, "Close test," 117.
,, cylinder, Viscosity of, 117.
,, Fatty lubricating, 114.
,, ,, acid in, 116.
,, for different classes of bearings, 116.
,, lubricating, Flashing point of, 117.
,, ,, Mixed, 118.
,, Mineral lubricating, 117.
,, Sulphuric acid in, 116.
,, Viscosity of, 115.
Olive oil, 115.
Oolitic limestone, 5.

Open hearth process, 146.
,, ,, Basic, 146.
"Open test" for oils, 118.
Optical pyrometer, 83.
Ore, Black band, 128.
,, Bog iron, 127.
,, Calcination of copper, 156.
,, concentration, Gold, 210.
,, dressing, 124.
,, furnace slag, 158.
,, Grey copper, 154.
,, Preparation for smelting iron, 129.
,, "Purple," 166.
,, Red copper, 154.
,, ,, zinc, 181.
,, Specular iron, 127.
Ores, Calcination of, 124.
,, Classification of, 123.
,, Copper, 154.
,, Iron, 126.
,, lead, Preparation of, for smelting, 171.
,, Mixed, 123.
,, nickel, Sudbury, Analysis of,
,, of aluminium, 218.
,, of lead, 170.
,, of manganese, 224.
,, Reduction of, 125.
,, Refining of, 125.
,, Roasting, 124.
,, ,, zinc, 182.
,, Self-reduction of, 125.
,, Silver, 202.
,, Sudbury treatment of nickel, 193.
,, Tin, 185.
,, ,, Dressing, 185.
,, ,, Roasting, 186.
,, Zinc, 181.
Orthoclase, 4.
Osmiridium, 216.
,, for pens, 217.
Oven, Coke, 53.
Overheating steel, 153.
Oxidation of metals difficult of reduction, 218.
,, of zinc, Heat of, 86.
Oxide of zinc, 181.
Oxygen, dissolved, Corrosive action of, 105.
,, in copper, 20.
,, manufacture, 75.
,, process, Brin's, 75.
,, ,, Kassner's, 76.

P

Paints for iron, 44.
Palladium, Melting point of, 82.
Parkes process for desilverising, 178.
,, ,, Plant for, 179.
"Parting" gold, 215.
,, of gold, Electrolytic, 216.
"Patent" fuel, 56.
Patera's process for silver, 208.
Patina of bronze, 41.
Pattinson's desilverising lead process, 177.
,, process, "high" system, 177.
,, ,, Improving lead by, 178.
,, ,, "low" system, 177.
,, ,, Use of steam in, 178.
Peat, Calorific value of, 56.
,, Composition of, 56.
Peaty waters, 101.
,, ,, Analyses of, 101.
Pens, Osmiridium for, 217.
Percentage of lead in crude zinc, 184.
Permanency of structural materials, 31.
"Permanent hardness" of water, 100.
Peroxide of sodium, 226.
Petroleum, Solidified, 58.
Pewter, 180.
Pewterer's solder, 37.
Phosphor bronze, 22.
,, ,, Composition of, 170.
Phosphoric pig, 137.
Pig, basic, Analysis of, 146.
,, Bessemer, 143.
,, boiling, 140.
,, iron, 135.
,, ,, Foundry, 14.
,, Phosphoric, 137.
"Pimple" metal, 159.
Pipes, Glass lined, 44.
Pipe stoves, 132.
Pitting of boiler plates, 107.
Planté cell, 91.
Plant for Parkes process, 179.
Plating gold, 216.
Platinoid, 197.
Platinum arsenide, 217.
,, iridium, 218.
,, Melting point of, 82, 217.
,, native, Analysis of, 216.
,, rhodium, 218.
,, Specific gravity of, 217.
,, Uses of, 217.
,, Winning of, 217.
Plumber's solder, 37.
"Pointed boxes," 212.
Polarisation, 86.
"Poling" copper, 160.

Polybasite, 202.
Porosity of stone, 32.
Porter-Clark process, 110.
Portland cement, 10.
,, stone, 5.
Potassium, Boiling point of, 226.
,, bromide, Melting point of, 82.
,, chloride, Melting point of, 82.
,, compound with carbon monoxide, 226.
,, iodide, Melting point of, 82.
,, Melting point of, 226.
,, Preparation of, 226.
,, sodium alloy for thermometers, 226.
,, Specific gravity of, 226.
,, sulphate, Melting point of, 82.
Power, Tidal, 95.
Precipitation of gold, 214.
,, process for lead, 175.
Preparation of brass, 169.
,, of iron ore for smelting, 129.
Preservation of iron, 43.
,, of stone, 43.
,, of structural materials, 42.
,, of timber, 45.
Primary cell, 90.
"Priming" in boilers, 112.
Principles of dry process for copper, 155.
,, of iron extraction, 129.
Producer gas, 63.
,, Analysis of, 65.
,, Calorific value of, 65.
Protection of boiler plates, 108.
Proximate analysis of coal, 52.
Puddled bar, 15.
,, ,, Analysis of, 141.
,, iron, Structure of, 142.
,, steel, 142.
Puddling, Chemistry of, 141.
,, Dry, 140.
,, Mechanical, 141.
Purbeck stone, 5.
Purification, Electrolytic, of iron, 147.
,, of mercury, 201.
"Purple" ore, 166.
Puzzuolana cement, 10.
Pyrites, Cobalt, 198.
,, Copper, 154.
,, cupriferous, Extraction of copper from, 166.
,, Iron, 129.
Pyrites, iron, Nickeliferous, 193.
,, matte, Collection of Gold in, 214.
,, spent, Extraction of copper from, 165.
,, Tin, 185.
Pyrolusite, 224.
Pyrometer, Calorimetric, 85.
,, Electrical resistance, 83.
,, Optical, 83.
,, Thermo-electric, 84.
,, Wedgwood's, 80.
,, Wiborgh's, 81.
Pyrometers, Gas, 80.

Q

Quartation, 216.
"Quickening" mercury, 213.

R

Rain water, 101.
Rape oil, Viscosity of, 115.
Reactions in blast furnace, 134.
Recalescence, 151.
Red antimony, 188.
,, bricks, 6.
,, copper ore, 154.
,, hæmatite, 127.
,, metal, 21.
,, zinc ore, 181.
Reduction, Chemical, of aluminium, 219.
,, Chemical, of magnesium, 223.
,, Electrolytic, of aluminium, 220.
,, ,, of magnesium, 223.
,, of antimony, by iron, 189.
,, of iron, 130.
,, of lead by carbon, 175.
,, ,, iron, 175.
,, of nickel oxide, 196.
,, of ores, 125.
,, of tinstone, 186.
,, of zinc, Thermal data for, 182.
Refinery copper slag, 160.
,, hearth, 139.
Refining antimony, 190.
,, Basic, for copper, 161.
,, bismuth, 192.
,, crude tin, 187.
,, electrolytic of copper, Current density for, 167.

Refining, Gold, 215.
,, ,, antimony sulphide, Process for, 215.
,, ,, Miller's chlorine, Process for, 215.
,, ,, sulphur, Process for, 215.
,, of copper electrolytically, 166, 167.
,, of lead electrolytically, 180.
,, of ores, 125.
,, of silver, 209.
,, process for bismuth, Matthey's, 192.
Refractory bricks, 9.
Regenerative heating, 67.
Regulus, "Close," 161.
,, of antimony, 189.
Retorts, zinc, Belgian, 182.
,, ,, Silesian, 183.
Reverberatory roasting furnace for copper, 156.
Rhodium-platinum, 218.
"Riffles," 211.
"Rich pot," 177.
Roaster slags, 159.
Roasting furnace for copper, Reverberatory, 156.
,, iron ores, 130.
,, ores, 124.
,, tin ores, 186.
,, zinc ores, 182.
Roman cement, 10.
Roofing materials, 25.
Rosin grease, 120.
"Rubber" gold, 212.
Ruby silver ore, 202.
Russell process for silver, 209.
Rust, Analysis of, 40.
"Rust joint," 38.
Rusting by galvanic action, 40.
Rusting of iron, 39.

S

SALINE waters, Corrosive action of, 105.
Salinometer, 102.
Sandstone, 1.
Schists, Cupriferous, 154.
Sclerometer, Turner's, 30.
Scorification for purifying copper, 160.
Scotch hearth for lead, 174.
Sea water, Analysis of, 102.
Secondary cell, 90.
,, ,, plates, 91.
Selenide of silver, 202.
Self-reduction of antimony, 189.
,, ,, of fine metal, 159.
,, ,, of lead, 172.
,, ,, of ores, 125.
Semi-water gas, 71.
,, ,, Calorific value of, 72.
,, ,, Composition of, 72.
,, ,, Use of, in gas engine, 73.
Senarmontite, 188.
Separation of cobalt from nickel speiss, 196.
Separators, Magnetic, 130.
Serpentine, 4.
,, Analysis of, 5.
Shear steel, 148.
Shot, 181.
Siemens-Halske electrolytic copper process, 166.
Siemens-Martin process, 146.
Siemens process, 146.
Silesian zinc retorts, 183.
Silicate of zinc, 181.
Silicon bronze, Composition of, 170.
,, carbide, 78.
Silver, Augustin's process for, 209.
,, Barrel process for, 206.
,, bromide, 203.
,, cadmium electroplating, 209.
,, Cement, 208.
,, chloride, 202.
,, ,, Solubility of, in salt solution, 208.
,, Claudet process for, 208.
,, Cupellation of lead for, 204.
,, Dry processes for, 204.
,, Extraction of, by copper matte as a solvent, 205.
,, ,, ,, by lead as a solvent, 204.
,, ,, ,, by mercury as a solvent, 206.
,, ,, ,, by wet processes, 206.
,, German, 197.
,, in galena, 107.
,, iodide, 203.
,, Kiss process, 208.
,, Mansfeld process for, 162.
,, Melting point of, 82, 209.
,, Mexican process for, 206.
,, Native, 202.
,, ore, Brittle, 202.
,, ,, Light red, 202.
,, ,, Ruby, 202.
,, ores, 202.
,, Patera's process for, 208.
,, Refining of, 209.

Silver, Russell process for, 209.
„ selenide, 202.
„ solder, 36.
„ Sources of, 203.
„ Specific gravity of, 205.
„ Sterling, 209.
„ sulphide, 202.
„ telluride, 202.
„ Uses of, 209.
„ Washoe process for, 206.
„ Winning of, 203.
"Silvering" looking glasses, 202.
"Singles," 189.
Slag, blast furnace, Composition of, 133.
„ cement, 10.
„ Copper refinery, 160.
„ in wrought iron, 15.
„ Lead, 175.
„ Metal, 159.
„ Ore furnace, 158.
„ wool, 133.
Slags, Roaster, 159.
Slate, 25.
Slimes, Gold, 212.
Smaltine, 197.
Smelting galena, Classification of methods of, 172.
„ „ Furnace for, 173.
„ Preparation of iron ore for, 129.
„ „ of lead ores for, 171.
Smoke and economy, 68.
„ prevention, 68.
Soapstone bricks, 8.
Sodium aluminium chloride, 220.
„ Boiling point of, 226.
„ Castner's process for, 225.
„ chloride, Electrolysis of, 226.
„ „ Melting point of, 82.
„ Distillation of, 225.
„ Melting point of, 226.
„ peroxide, 226.
„ potassium alloy for thermometers, 226.
„ preparation, Castner's process, 225.
„ Reduction of, by carbon, 225.
„ Specific gravity of, 226.
„ sulphate, 82.
„ tungstate, 186.
„ Vautin's process for preparation of, 226.
Softening lead, 176.
„ water by barium chloride, 111.
„ „ by caustic soda, 110.
„ „ by heating, 108.
„ „ by lime, 109.
Softening water by magnesia, 111.
„ „ by sodium carbonate, 110.
„ „ „ fluoride, 111.
„ „ in the boiler, 111.
Soft solder, 37.
„ waters, 101.
Solder, 180.
„ Coarse, 37.
„ Fine, 37.
„ Melting point of, 181.
„ Pewterer's, 37.
„ Plumber's, 37.
„ Tinman's, 37.
Soldering, 36.
„ Aluminium, 222.
„ Autogenous, 34.
„ Fluxes for, 37.
„ Hard, 36.
Solid depolariser, 88.
„ lubricants, 119.
Solidified petroleum, 58.
Solidifying point of mercury, 202.
Solubility of lead in zinc, 178.
„ of silver chloride in salt solution, 208.
„ of zinc in lead, 178.
Sources of bismuth, 191.
„ of energy, 48.
„ of gold, 209.
„ of magnesium, 223.
„ of mercury, 198.
„ of nickel, 193.
„ of silver, 203.
„ of zinc, 181.
Spathic iron ore, 128.
„ „ Analyses of, 128.
Specific gravity of aluminium, 222.
„ of antimony, 190.
„ of bismuth, 192.
„ of cadmium, 185.
„ of cement, 11.
„ of cinnabar, 198.
„ of coals, 50.
„ of cobalt, 198.
„ of galena, 171.
„ of gold, 216.
„ of iron, 149.
„ of lead, 180.
„ of magnesium, 223.
„ of manganese, 224.
„ of mercury, 202.
„ of nickel, 197.
„ of platinum, 217.
„ of potassium, 226.
„ of silver, 209.
„ of sodium, 226.
„ of steel, 153.

Specific gravity of steel, Effect of hardening on, 153.
„ of tin, 187.
„ of tin stone, 185.
„ of zinc, 184.
Specific heat of aluminium, 223.
Specular iron ore, 127.
Speculum metal, 188.
Speiss cobalt, 197.
„ nickel, 196.
„ „ Separation of cobalt from, 196.
Spelter, 36.
„ (cast zinc), 184.
Spent pyrites, Extraction of copper from, 165.
Sperm oil, Viscosity of, 115.
Sperrylite, 217.
Spiegel-eisen, 137.
Spindle oil, Viscosity of, 117.
"Spirits of salt killed," 37.
Spray maker, 57.
"Spurstein," 163.
Stack of blast furnace, 130.
Stages of Bessemer blow, 144.
Stamps for gold, 211.
Standard of viscosity, 115.
„ gold, Composition of, 216.
Stannic oxide, 185.
"Starbowls," 189.
"Starring," 190.
Steam in Pattinson process, Use of, 178.
„ raising, Chemistry of, 98.
Steatite bricks (see *Soapstone*), 8.
Steel, basic, Analyses of, 146.
„ Bessemer, Analysis of, 143.
„ Blister, 147.
„ castings, Composition of, 19.
„ Cause of hardness in, 152.
„ cement, Production of, 147.
„ Chromium, 19, 152.
„ Commercial grades of, 153.
„ „ „ Percentage of carbon in, 153.
„ crucible, Analysis of, 148.
„ „ Cast, 148.
„ Crystalline structure of, 153.
„ Double shear, 148.
„ Hardening, 150.
„ „ effect on tensile strength, 153.
„ Influence of impurities on, 148.
„ Manganese, 20, 152.
„ Mild, 15, 18.
„ Nickel, 19, 152.
„ „ Effect of cooling on, 152.
„ Overheating, 153.
„ Shear, 148.
Steel, Specific gravity of, 153.
„ „ „ Effect of hardening on, 153.
„ Tempering, 150.
„ Tungsten, 152.
„ Tyre, Analysis of, 147.
Steels, Analysis of, 18.
„ Specific gravity of, 19.
Step grate kiln, 55.
Stereotype, 181.
Sterling silver, 209.
Stock bricks, 6.
Stone, Bath, 5.
„ Effect of frost on, 32.
„ Lichens on, 33.
„ Porosity of, 32.
„ Portland, 5.
„ Preservation of, 43.
„ Purbeck, 5.
Stones, 1.
„ Calcareous, 1, 4.
„ Siliceous, 1.
Stonesfield slates, 25.
Storage cell, 90.
Stourbridge bricks, 7.
Stove, Cowper, 131.
„ Hot-blast, 131.
Stoves, Pipe, 132.
Strata, Water-yielding, 99.
Stream tin, 185.
Strength of structural materials, 29.
Structural materials, Chemical attack of, 38.
„ „ Permanency of, 31.
„ „ Preservation of, 42.
„ metals, 13.
Structure of puddled iron, 142.
"Stupp," 201.
Subsidence of precipitates in softened water, 112.
Sudbury nickel ores, Analysis of, 194.
„ „ „ Treatment of, 194.
Sulphide of antimony, 188.
„ „ Liquation of, 188.
„ „ process for refining gold, 215.
„ of lead, 170.
„ of mercury, 198.
„ of silver, 202.
„ of zinc, 181.
Sulphuric acid in oils, 116.
Sulphur process for refining gold, 215.
Sun's energy, 96.
Syenitic granite, 3.

T

Telluride of silver, 202.
Temperature, Influence of, on viscosity, 115.
„ Measurement of, 78.
„ of hot blast, 132.
„ Working, for zinc, 184.
Temperatures, Industrial, 85.
Tempering steel, 150.
"Temporary hardness" of water, 100.
Tensile strength of cast iron, 14.
„ „ of cement, 13.
„ „ of ingot iron, 19.
„ „ of magnesium, 224.
„ „ of wrought iron, 16.
"Test," 205.
Test, Brard's, 32.
„ piece, Contraction of area of, 17.
„ „ Elongation of, 17.
Testing cement, 11.
„ machine, 17.
„ „ for cement, 12.
Tests for brass, 22.
„ of hardness, 31.
Thermal data for reduction of zinc, 182.
Thermo-electric pyrometer, 84.
Thermometers, 79.
„ Potassium-sodium alloy for, 226.
Thomas-Gilchrist process, 145.
Throat of blast furnace, 130.
Tidal power, 95.
Tiles, 25.
Timber, Preservation of, 45.
Tin amalgam, 188.
„ Common, 187.
„ crude, Impurities in, 187.
„ Disintegration of, by cold, 188.
„ foil, 188.
„ Grain, 187.
„ Grey, 188.
„ Melting point of, 187.
„ ores, 185.
„ „ Dressing, 185.
„ „ Roasting, 186.
„ „ Tungsten in, 186.
„ plate, 27.
„ pyrites, 185.
„ Refining crude, 187.
„ Specific gravity of, 187.
„ stone, 185.
„ „ Reduction of, 186.
„ „ Specific gravity of, 185.
„ Uses of, 187.
„ white cobalt, 197.
„ Winning of, 185.
„ Working temperature for, 187.
Tinman's solder, 37.
Tinned copper, 41.
„ iron, 27.
Titanium compound in blast furnace, 135.
Tossing tub, 212.
Toughening copper, methods used, 161.
"Tough-pitch" copper, 160.
Transmission of energy, 97.
Trap, 4.
Treatment of nickel ores at Sudbury, 194.
Tube, "Compo.," 181.
Tungstate of sodium, 186.
Tungsten in tin ores, 186.
„ „ steel, 152.
Turner's sclerometer, 30.
Twyers of blast furnace, 131.
Type metal, 181.
Tyre steel, Analysis of, 147.

U

Uses of aluminium, 222.
„ of antimony, 190.
„ of bismuth, 192.
„ of cobalt, 198.
„ of gold, 216.
„ of magnesium, 223.
„ of mercury, 201.
„ of nickel, 197.
„ of platinum, 217.
„ of silver, 209.

V

"Valvolene," 118.
Vanner, Frue, 213.
Vautin's process for preparation of sodium, 226.
Viscosity, Influence of temperature on, 115.
„ of castor oil, 115.
„ of cylinder oil, 117.
„ of lard oil, 115.
„ of machinery oil, 117.
„ of neatsfoot oil, 115.
„ of oils, 115.
„ of olive oil, 115.
„ of rape oil, 115.
„ of sperm oil, 115.
„ of spindle oil, 117.
„ Standard of, 115.

W

Wad, 224.
Washoe process for silver, 206.

Waste of fuel by boiler incrustation, 104.
Water, Bicarbonates in, 99.
„ Calcium sulphate in, 99.
„ ferruginous, Softening of, 110.
„ gas, Analysis of, 71.
„ „ Calorific value, 71.
„ „ Hydrogen from, 93.
„ „ producer, 70.
„ "Hard," 100.
„ in axle grease, 120.
„ Magnesium chloride in, 102.
„ "Permanent hardness" of, 100.
„ power, 94.
„ „ Electrical transmission of, 94.
„ Rain, 101.
„ softened, Subsidence of precipitates in, 112.
„ softening by barium chloride, 111.
„ „ by caustic soda, 110.
„ „ by heating, 108.
„ „ by lime, 109.
„ „ by magnesia, 111.
„ „ by sodium carbonate, 110.
„ „ „ fluoride, 111.
„ „ in the boiler, 111.
„ "Temporary hardness" of, 100.
„ yielding strata, 99.
Waters, Classification of, 98.
Wedgwood's pyrometer, 80.
Welding, 35.
„ Electrical, 35.
Welsbach light, 73.
Welsh copper process, Diagram of, 161.
„ process for copper, 155.
„ „ „ analyses of products, 162.
"Werk-blei," 176.
Wet extraction, 124.
„ „ of bismuth, 192.
„ „ of copper, 165.
„ processes for extraction of silver, 206.
Whinstone, 4.
White iron, 135.
„ „ Analysis of, 136.
„ „ Specific gravity of, 136.
"White metal," 159.
White metals, 23, 181.
"Whitening" iron, 139.
White, Tin, cobalt, 197.
Wiborgh's pyrometer, 81.
Willemite, 181.
Wind energy, 95.
Winning, Electrolytic, of antimony, 190.
„ „ of copper, 166.
„ of aluminium, 219.
„ of antimony, 188.
„ of bismuth, 191.
„ of copper by dry process, 154.
„ of gold, 210.
„ of magnesium, 223.
„ of manganese, 224.
„ of mercury, 198.
„ of nickel, 193.
„ of platinum, 217.
„ of silver, 203.
„ of tin, 185.
„ of zinc, 182.
„ „ electrolytically, 184.
Wolfram, 186.
Wood as fuel, 56.
„ Calorific value of, 56.
„ Charred, 47.
„ creosote, 46.
„ „ Analysis of, 47.
Wood's metal, 193.
Working temperature for magnesium, 223.
„ „ „ zinc, 184.
"Work-lead," 176.
"Workstone," 174.
Wrought iron, 15.
„ „ Analysis of, 16, 141.
„ „ Influence of impurities on, 16.
„ „ Tensile strength of, 16.
„ „ Yield point of, 18.

Y

Yellow metal, 22.
"Yield point," 17.
„ „ of wrought iron, 18.
Yorkshire flagstone, 2.

Z

Zinc alloys, 184.
„ amalgam, 179.
„ Amalgamated, 89.
„ as a source of energy, 89.
„ Boiling point of, 82, 182.
„ carbonate, 181.
„ „ Basic, 181.
„ Cast, spelter, 184.
„ Corrosion of, 41.

Zinc, crude, Impurities in, 184.
„ Distillation of, from ore, 183.
„ dust, 184.
„ Electrolytic winning of, 184.
„ fume, 182.
„ Heat of oxidation of, 86.
„ iron alloys, 184.
„ Melting point of, 82, 184.
„ ore, Red, 181.
„ ores, 181.
„ „ Roasting, 182.
„ oxide, 181.
„ Percentage of lead in crude, 184.
Zinc, retorts, Belgian, 182.
„ „ Silesian, 183.
„ silicate, 181.
„ Solubility of lead in, 178.
„ Sources of, 181.
„ Specific gravity of, 184.
„ sulphide, 181.
„ Thermal data for reduction of, 182.
„ Uses of, 184.
„ Winning of, 182.
„ Working temperature for, 184.
Zinced iron, 26.
Zinceisen, 184.

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